XRF Analyses of Soils Taken From the Warwick Mountain Area, Cobequid Highlands, Nova Scotia

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Introduction

Nova Scotia Department of Natural Resources geological mapping fieldwork during the field season of 2011-2012 by MacHattie and White (2014) resulted in the discovery of several anomalous gold concentrations in the Cobequid Highlands. Two of the most anomalous of these samples were found in the immediate vicinity of Warwick Mountain, Colchester County (T. G. MacHattie, unpub. data, 2014). Warwick Mountain is on the north side of the east-west-oriented Cobequid Highlands, which were originally formed as part of a long chain of mountainous terrain that marked the continental suture between Avalonia and its foreland basin during the Middle to Late Devonian Acadian Orogeny.

Regional Geology

Mapping in the Warwick Mountain region is within a larger region defined by MacHattie and White (2014). For the purpose of this study, the regional geology is described as the region marked by the Hart Lake—Byers Lake Pluton contact with the Byers Brook Formation in the south to Highway 256 in the north, and by Earltown in the east to Byers Lake in the west (Fig. 1). This area is composed of two distinct tectonic blocks as described by MacHattie and White (2014) as the Bass River and Jeffers blocks. However, rocks in the Warwick Mountain area, the focus of this study, are all found within the Jeffers block, and so the Bass River block will not be described here (Fig. 1).

Regionally at Warwick Mountain, rocks within the Jeffers block include the Dalhousie Mountain Formation of the Jeffers Group, the Wilson Brook Formation, the Byers Brook and Diamond Brook formations of the Fountain Lake Group, and the plutonic Hart Lake—Byers Lake Pluton (Fig. 1).

Local Geology

Locally, rocks at Warwick Mountain consist of dacitic to andesitic, crystal to lithic tuffs and rhyolitic volcanics of the late Neoproterozoic Dalhousie Mountain Formation, which is overlain unconformably by fine metasedimentary siltstones and shales of the Silurian Wilson Brook Formation, which in turn is in faulted contact with Late Devonian to Carboniferous basaltic flows, minor rhyolitic flows, and interbedded sand and siltstones of the Diamond Brook Formation (MacHattie and White, 2014; Fig. 1). The Diamond Brook formation forms the underlying bedrock in the grid area. This formation consists of volcanic rocks that are interpreted to have formed as part of a continental rifting environment (MacHattie and White, 2014), implying a mantle-derived magmatic source. ²⁰⁶Pb/²³⁸U age dates for these rocks are 355-358±3 Ma.

Samples taken in the Warwick Mountain area as part of the mapping program by MacHattie and White (2014) returned anomalous gold values in two samples (S104 and S441; T. G. MacHattie, unpub. data, 2014).

Surficial geology for the Warwick Mountain area has been shaped by four phases of ice flow over this area of Nova Scotia. This has resulted in two main layers of till. The lower till consists of a mostly locally derived, stony, hybrid till reflecting an early east-southeast flow that later developed into a south-southeast ice-flow direction (Stea and Mott, 1990). This was followed by a second ice-flow phase that was due south. This till is overlain by a finer, silty-sandy to clayey hybrid till

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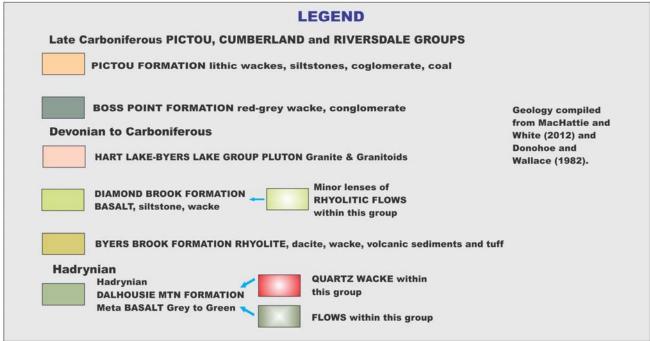


Figure 1. Regional geology map for Warwick Mountain area. Geology compiled from MacHattie and White (2014) and Donohoe and Wallace (1982).

with clasts and elements that were dispersed from rocks south of Warwick Mountain reflecting a phase of northerly ice flow, as described by Stea and Mott (1990) (Fig. 2).

Methods

Geochemical samples taken in the Warwick Mountain area during the mapping program by MacHattie and White (2014) returned anomalous gold values in two samples (S104 and S441; T. G. MacHattie, unpub. data, 2014), which were re-sampled as part of this study (Fig. 3). These were augmented by a loose soil grid over the area extending mostly south and up-topography over the locality.

The Warwick Mountain area was selected for study partly due to the proximity of an anomalous stream sediment S104 (T. G. MacHattie, unpub. data, 2014). This sample implies that the source for the anomaly is within the catchment basin upstream, and hence up-topography, from the sample site. Furthermore, the upper hybrid till from which soil in the Warwick Mountain area is derived is believed to have been dispersed north from the Cobequid Highlands, located to the south, as described by the third ice-flow phase described by Stea and Mott (1990).

Sample location data such as angle of slope, clast size, depth and colour were recorded at each site. Samples were sieved at -20 mesh and placed in baggies for analysis by an Innovative XRF Technologies Olympus X-5000 Mobile XRF System owned by the Nova Scotia Department of Natural Resources. The analyses were entered into a worksheet with location data and had minimal filtering to allow for image creation by a contouring package. The images were contoured as three-dimensional wireframes using Surfer. Correlations between elements were also investigated by performing a Spearman rank correlation coefficient analysis on the dataset.

Results

A plot was created for the colour data for each sample (Fig. 4). Colour data reveal that soils at

Warwick Mountain are closely related to topographic elevation. Analysis plots for potassium (Fig. 5a) and calcium (Fig. 5b) are elevated in areas coincident with one another. This pattern is also reflected in plots for zirconium (Fig. 5c), copper (Fig. 5d), lead (Fig. 6a), chromium (Fig. 6b) and nickel (Fig. 6c). Weak correlations with barium (Fig. 6d), rubidium (Fig. 7a), thorium (Fig. 7b), yttrium (Fig. 7c) and iron (Fig. 7c) are also present. The titanium (Fig. 8a) and vanadium (Fig. 8b) plots were relatively flat, but there exists a single high value on the western margin of the grid for both elements. Two elevated manganese (Fig. 8c) analyses are present on the east-southeast margin of the grid and in the central western locality as well. Arsenic (Fig. 8d) displays an anomaly in the central eastern part of the grid as well as along the southsouthwest margin. The plot for zinc (Fig. 9a) exhibits a largely flat pattern with a single high value in the southwest corner of the grid. A single high niobium (Fig. 9b) value is displayed in the centre of the grid for that element.

A table of Spearman rank correlation coefficient values is presented in Table 1. Values revealed several very strong correlations as well as some strong ones.

Potassium has a very strong correlation to rubidium (0.92). Other strong correlations are calcium to strontium (0.70), vanadium to titanium (0.80), titanium to iron (0.75) and iron to vanadium (0.88). Niobium has a moderately strong correlation to titanium (0.53), as well as to vanadium (0.47) and arsenic (0.45). These elements all show relatively strong correlations to one another and to iron.

Moderately strong correlations are noted between base metal elements such as copper, lead, zinc, nickel, iron and manganese.

Iron reflects a negative correlation to rubidium (-0.43). A negative correlation is also reflected between zirconium and zinc (-0.45) and nickel (-0.40).

Correlations with barium include potassium (0.62) and rubidium (0.47). Barium also exhibits an

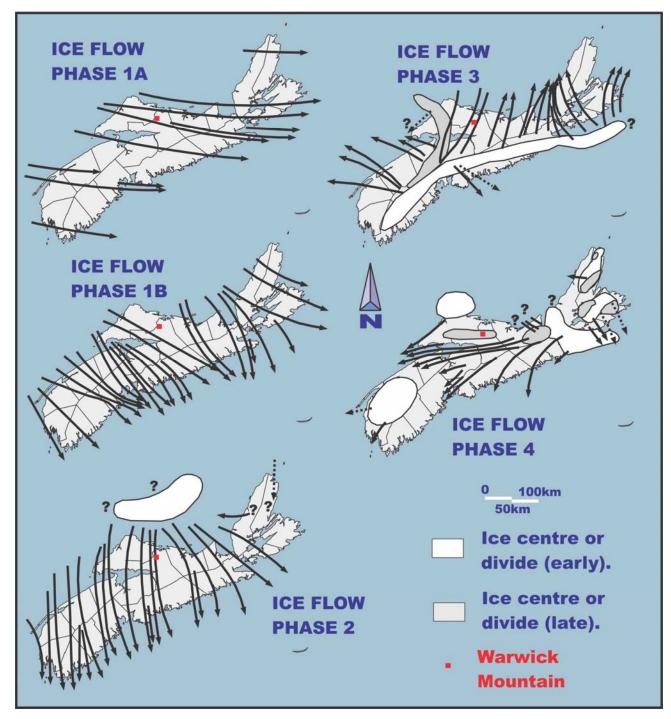


Figure 2. Ice flow phases for Nova Scotia. Modified slightly from Stea and Mott (1990).

inverse correlation with chlorine (-0.32). Chlorine exhibits positive correlations with titanium (0.33), vanadium (0.41), iron (0.51) and niobium (0.4).

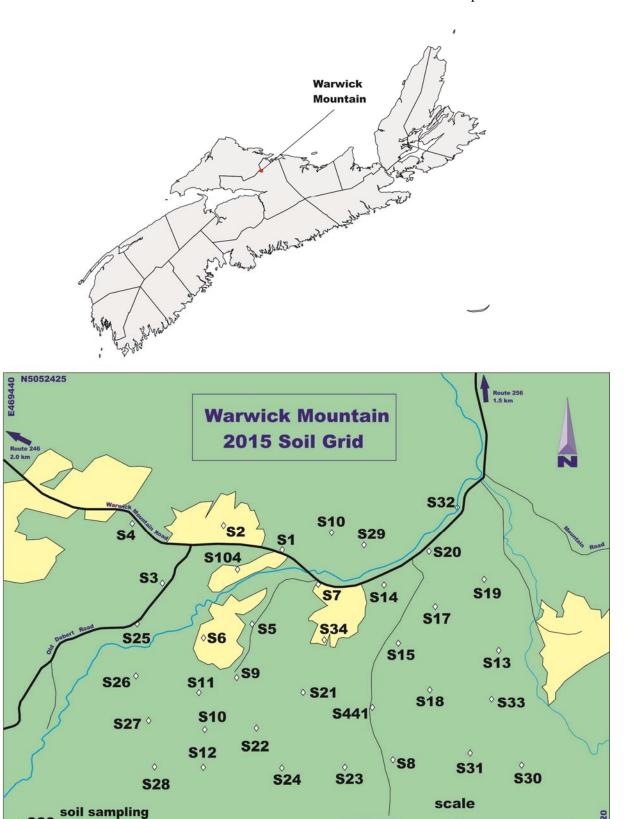
Discussion

The soil plot (Fig. 4), which reflects topography at Warwick Mountain, exhibits the hybrid till

development in the area, as well as the dendritic drainage pattern, which has resulted in fluvial excavation of the till in the area. Soil development is, therefore, closely related to till structure on Warwick Mountain. The tills, though hybrids, are in part a reflection of the bedrock in the area and most are derived from the underlying Diamond Brook Formation.

1km

N5050220



0

250m

500m

Figure 3. Warwick Mountain soil sample grid map.

cultivated ground

location

⋄ S28

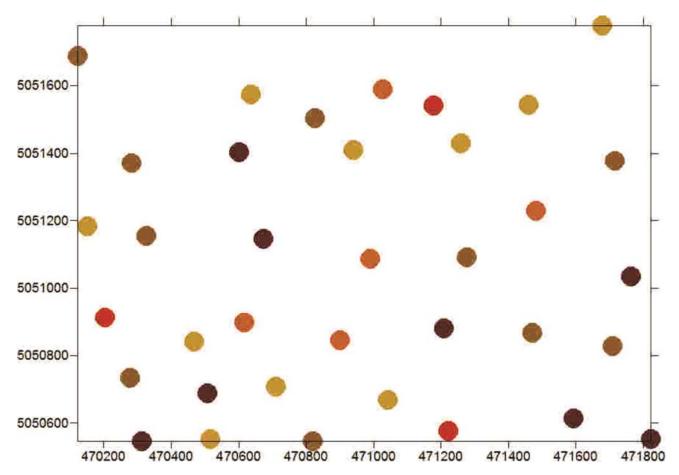


Figure 4. Warwick Mountain soil colour map.

The plots for potassium and calcium coincident to one another are in areas of elevated topography and reflect alteration in resistant volcanic bedrock. A weaker plot pattern is seen with respect to zirconium, copper, lead, chromium and nickel. Barium, rubidium, thorium, yttrium and iron are magmatic-related elements, some mafic and some felsic. The titanium, vanadium and iron anomaly on the southwestern margin of the grid is believed to reflect mafic influence on these elements at the rhyolite-basalt contact. The two elevated manganese values are somewhat more enigmatic and may reflect late stage emplacement alteration as well as ferromagnesian relationship to iron. The arsenic anomaly in the central eastern part of that grid is not surprising. Nearby drilling by an exploration company (Jensen, 2012) was located where arsenopyrite was noted in surface bedrock exposure (MacHattie, pers. comm., 2016). The single zinc anomaly is coincident with massive sulphide mineralization found in outcrop near this sample on the last day of fieldwork at Warwick Mountain and

will be revisited as an extended part of this study in 2016. The single, high niobium value is an anomaly that cannot be explained at this time.

The Spearman rank correlations between potassium and rubidium as well as calcium and strontium are all natural ones, reflecting felsic associations to bedrock sources.

Potassium and rubidium are alkaline elements and therefore are highly reactive. Calcium and strontium have the same number of electrons in their outer shells and, as alkaline earth elements, will form strong correlations to one another if they are found together as they bond with other elements. The correlations amongst vanadium, titanium and iron can be explained through the formation of titanium and iron-based minerals that are sympathetic to bonds with vanadium—namely magnetite and ilmenite. Both minerals are found in the area within the Warwick Mountain Formation and Fountain Lake Group.

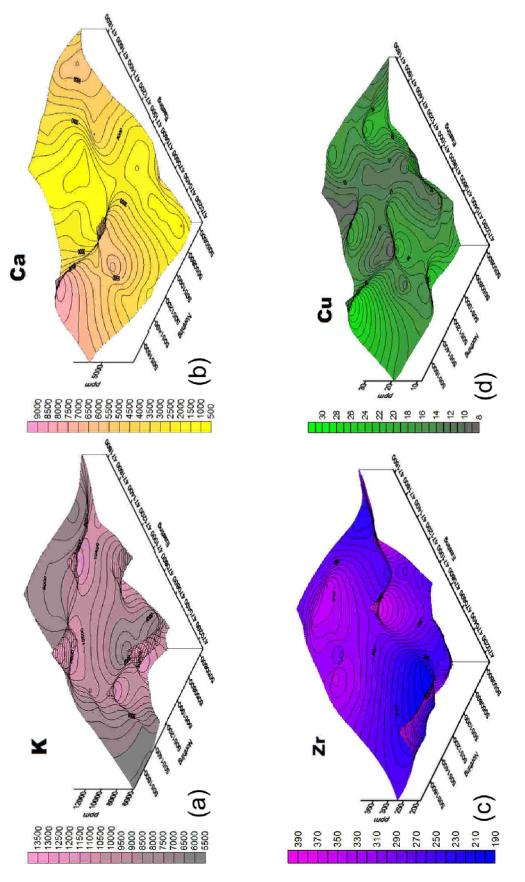


Figure 5. XRF soil analyses plots for K, Ca, Zr and Cu.

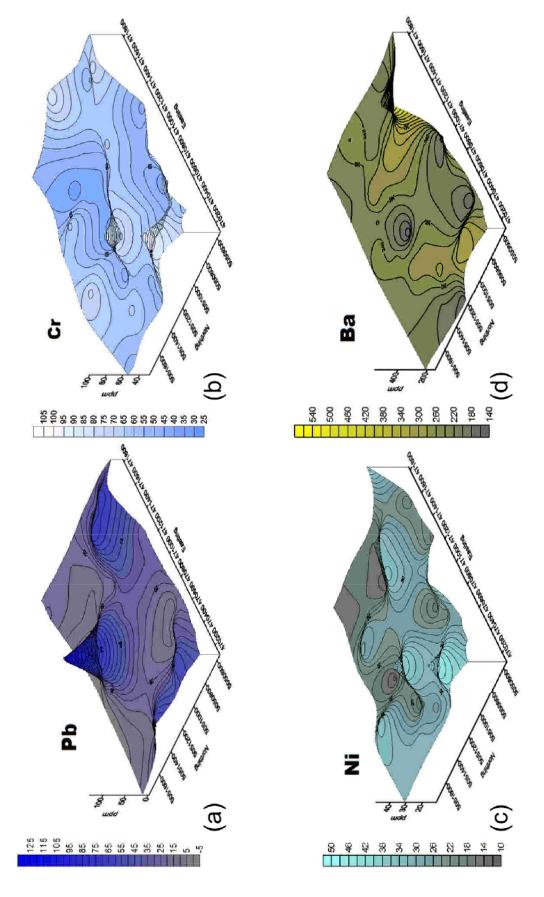


Figure 6. XRF soil analyses plots for Pb, Cr, Ni and Ba.

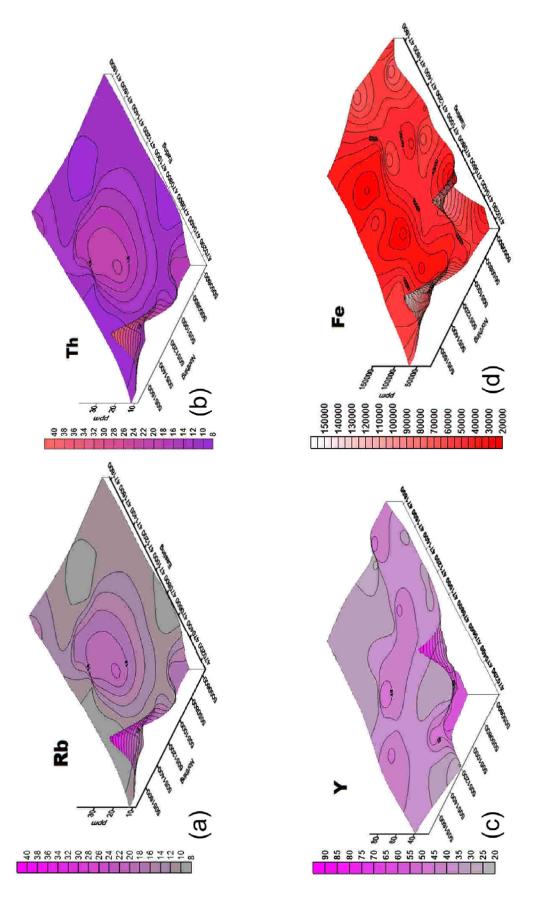


Figure 7. XRF soil analyses plots for Rb, Th, Y and Fe.

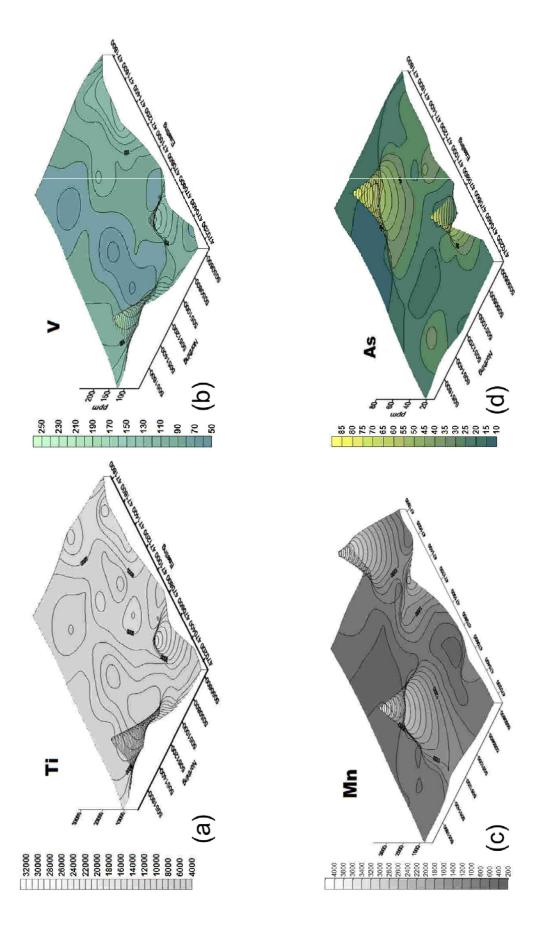
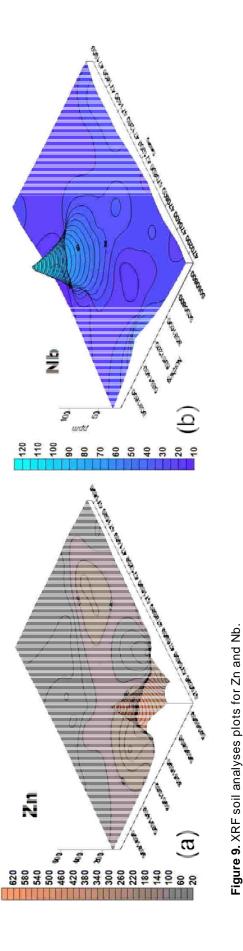


Figure 8. XRF soil analyses plots for Ti, V, Mn and As.



The correlations of lesser strength between chlorine and titanium (0.33), iron (0.51) and niobium (0.40)should be ignored as chlorine analysis by this portable XRF method are not reliable. Niobium is commonly found as a pegmatitic endmember of late-stage magmatic alteration associated with leucocratic rocks that are seen at Warwick Mountain as clasts in tills and as alluvial cobbles and gravel in streams draining the area. However, the correlation between niobium and titanium (0.53) as well as that of niobium and vanadium (0.80) could also suggest a more mafic influence to this element, or potentially the Nb may be hosted in titaniferous minerals such as rutile or ilmenite.

The moderately strong correlations between barium and potassium are worthy of note as both have been suggested as indicator elements for thorium as well as IOCG gold (MacHattie, 2013).

Barium's attractions to potassium and rubidium are natural, and this element usually forms minerals and alloys with other basic elements. The negative correlation with chlorine can be explained as a limitation of the analytical instrument with respect to the element chlorine as discussed earlier in the case of correlations between chlorine and other elements (MacHattie, pers. comm., 2016). These limitations must also be taken into account for the correlations between chlorine and titanium, vanadium, iron and niobium.

Moderately strong correlations for niobium with titanium, vanadium, arsenic and iron can be explained by mafic influence from gabbroic source rocks. The moderately strong correlations noted amongst base metal elements such as copper, lead, zinc, nickel, iron and manganese can likewise be attributed to mafic sources influencing till and soil within the study area.

The negative correlation of iron to rubidium and between zirconium and zinc as well as zirconium and nickel is a reflection of felsic influence on zirconium within the study area.

Recommendations

The grid should be extended farther south and specifically southwest to further investigate

Table 1. Spearman rank correlation coefficient table for Warwick Mountain XRF analyses.

| | Cl | × | Ca | Τi | > | Ċ | Mn | Fe | ï | Cn | Zn | As | Rb | Sr | Y | Zr | $^{\rm N}$ | Ba | Pb | Th | |
|----|----|---|------|------|------|-------|------|------|-------|------|-------|------|-------|------|--------|---------|------------|--------|--------|-------|----|
| Th | | | | | | | | | | | | | | | | | | | | 1.00 | Th |
| Pb | | | | | | | | | | | | | | | | | | | 1.00 | 0.22 | Ph |
| Ba | | | | | | | | | | | | | | | | | | 1.00 | 0.19 | -0.07 | Вя |
| Nb | | | | | | | | | | | | | | | | | 1.00 | -0.23 | 0.21 | 0.19 | ΔŊ |
| Zr | | | | | | | | | | | | | | | | 1.00 | 0.40 | -0.01 | -0.10 | 0.01 | 7r |
| Y | | | | | | | | | | | | | | | 1.00 | -0.01 | 0.12 | 0.29 | 0.38 | -0.06 | |
| Sr | | | | | | | | | | | | | | 1.00 | 60.0 | -0.50 | -0.31 | 0.45 (| | -0.11 | |
| | | | | | | | | | | | | | 00.1 | 0.20 | 0.59 0 | 0.19 | 0.16 | 0.47 0 | 0.26 0 | -0.02 | |
| Rb | | | | | | | | | | | | 0 | | | | | | | | | |
| As | | | | | | | | | | | | 1.00 | 0.21 | 0.15 | 0.27 | 5 -0.24 | 9 0.45 | -0.05 | 0.45 | 0.08 | |
| Zn | | | | | | | | | | | 1.00 | 0.63 | 0.23 | 0.31 | 0.41 | -0.45 | -0.09 | 0.19 | 0.43 | 0.13 | Zn |
| Cu | | | | | | | | | | 1.00 | 0.39 | 0.14 | -0.15 | 0.41 | 0.11 | -0.20 | -0.13 | 0.27 | 0.05 | -0.07 | ځ |
| Ni | | | | | | | | | 1.00 | 0.53 | 09.0 | 0.25 | -0.08 | 0.34 | 0.26 | -0.40 | -0.09 | 0.10 | 0.17 | 0.13 | Ņ. |
| Fe | | | | | | | | 1.00 | 0.35 | 0.31 | 0.31 | 0.52 | -0.43 | 0.26 | -0.12 | -0.26 | 0.35 | -0.16 | 0.26 | 90.0 | Fe |
| Mn | | | | | | | 1.00 | 0.54 | 0.34 | 0.34 | 0.51 | 0.34 | -0.16 | 0.35 | 0.19 | -0.35 | -0.01 | 0.25 | 0.44 | -0.04 | Mn |
| Cr | | | | | | 1.00 | 0.37 | 0.45 | 0.53 | 0.51 | 0.42 | 0.14 | -0.06 | 0.47 | 0.15 | -0.34 | -0.21 | 0.32 | 0.20 | -0.06 | ځ |
| Λ | | | | | 1.00 | 0.37 | 0.59 | 0.88 | 0.33 | 0.34 | 0.26 | 0.47 | -0.31 | 0.30 | -0.02 | -0.09 | 0.47 | 0.02 | 0.28 | -0.04 | Λ |
| Ti | | | | 1.00 | 08.0 | 0.11 | 0.32 | 92.0 | -0.06 | 0.13 | -0.15 | 0.27 | -0.47 | 0.07 | -0.25 | 0.18 | 0.53 | -0.22 | 0.04 | -0.08 | ï |
| Ca | | | 1.00 | | | 0.41 | | | | | | | | | | | | | | | |
| K | | | | | | -0.02 | | | | | | | | | | | | | | | |
| Cl | | | | | | 0.10 | | | | | | | | | | | | | | | |
| | | | | | | Cr | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | | | | | | |

anomalous elemental associations seen on the geochemistry plots in that direction. Pebble counts could help provide resolution to buried geological contact locations and to verify geology and any potential economic mineralization.

References

Donohoe, H. V. and Wallace, P. I. 1982: Geological map of the Cobequid Highlands, Colchester, Cumberland and Pictou counties, Nova Scotia. Map 82-8, Sheet 3 of 4, Scale 1:50,000.

Jensen, L. 2012: Drill Program Whirley Brook Lic# 09724 Colchester County, N.S. Sugarloaf Resources Inc. NTS: 11E11B; Nova Scotia Department of Natural Resources, Assessment Report ME 2012-077, 97 p. MacHattie, T. G. 2013: Newly recognized epithermal-style gold occurrences associated with late Devonian to early Carboniferous bi-modal volcanism in the northeastern Cobequid Highlands; Nova Scotia Department of Natural Resources, Report ME 2012-001, p 31-39.

MacHattie, T. G. and White, C. E. 2014: Preliminary geology of the eastern Cobequid Highlands, northern mainland Nova Scotia: *in* Nova Scotia Department of Natural Resources, Report ME 2013-001, 2013, p. 27-43.

Stea, R. R. and Mott, R. J. 1990: Quaternary geology of Nova Scotia: guidebook for field excursion, 1990; Nova Scotia Department of Natural Resources, Open File Report 90-008, 85 p.