



Catchment Analysis and Interpretation of Stream Sediment Data from QUEST South, British Columbia

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D.C. Arne, Associate, ioGlobal Solutions Inc, 300 – 1055 West Hastings Street, Vancouver, V6E 2E9 arne.dennis@gmail.com

E.B. Bluemel, Geochemist, ioGlobal Solutions Inc, 300 – 1055 West Hastings Street, Vancouver, V6E 2E9, britt.bluemel@ioglobal.net

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Page 1 of 25

Table of Contents

Summary	2
Introduction	
Geochemical Catchment Analysis	4
Methodology	5
Sample Location Validation	5
Exploratory Data Analysis	9
Data Presentation	
Additive Pathfinder Indices	16
RGB Analysis	
Multivariate Analysis	
Optimum Catchment Area	
Conclusions	
Acknowledgements	
References	23



Summary

Catchment analysis and interpretation of geochemical data have been undertaken for 9041 stream sediment samples from the QUEST South project area of southern British Columbia. The geochemical data consist of new analyses for 8536 archived regional geochemical samples (RGS) that were previously re-analyzed by Geoscience BC (Report 2010-4) using modern analytical methods and 785 new stream sediment samples collected to augment the existing RGS samples (Geoscience BC Report 2010-13). Catchments could not be calculated for 9 RGS samples (0.1 % of the samples).

A number of RGS sample locations were found to be inconsistent with the current 1:20,000 scale stream network and were "snapped" to the nearest stream and manually adjusted as necessary. Adjusted sample locations were validated against the original locations recorded on 1:50,000 topographic map sheets. Catchment basins for the samples were determined by the British Columbia Geological Survey using an in-house process. The catchment polygons were used to calculate the percentages of each bedrock lithological unit occurring in individual catchments. Raw and residual geochemical data were Z-score levelled by the dominant lithological unit in each catchment to correct for the effects of variable background on the geochemical data. Some elements (Ag, Hg, Mn, Na, Pb, S, Te, Tl) were found to show variability in data between the two laboratories undertaking the analyses in samples collected from the same geographic area. Data for these elements have been Z-score levelled for possible analytical variation. Exploratory data analysis indicates that some elements (Co, Cu, Ni, Cr, Sc, Zn, Sb, Ba, Ag, Mo, As) show positive correlations with either Fe or Mn, suggesting some degree of metal scavenging by secondary Fe or Mn oxides. Data for these elements have undergone robust regression analysis to calculate residuals for further analysis. The original RGS instrumental neutron activation analyses (INAA) for Au used average sample weights of 23 g and, along with INAA Au analyses for the 785 new samples, are the preferred Au data used for interpretation and plotting in this report.

A range of digital products accompany this report. These include a spreadsheet containing the compiled stream sediment data, catchment areas and dominant bedrock type, GIS files showing sample locations and catchments, a series of gridded geotiff images for raw, levelled and residual data for most elements, gridded pathfinder associations for a number of common mineral deposit types (orogenic Au, epithermal Au, base metals and porphyry Cu deposits) as geotiffs and pdf maps, and RGB thematic maps for these pathfinder associations. The levelled and residual data provide new insights into the regional stream sediment geochemical data, and reveal subtle trends and areas of elevated metal concentration that may warrant follow-up investigation.

QUEST-South Geochemistry



Page 3 of 25

Introduction

In 2009 archived historical regional geochemical stream sediment samples (RGS) from the QUEST-South project area (Figure 1) were re-analyzed by Geoscience BC (GBC) using modern analytical methods (Geoscience BC Report 2010-4). In-fill sampling of part of the QUEST-South project area was also undertaken in 2009 (Figure 1), and is described in Geoscience BC Report 2010-13. The locations of both sample groups are illustrated in Figure 2. Further value has been added to these data by undertaking catchment analysis of the region and exploratory data analysis (EDA) of the new geochemical results. Data treatment has been validated using known MINFILE deposits and occurrences within the project area to provide a robust interpretation of the data that highlights new areas of interest not evident through examination of the raw data.



Figure 1. Location of the QUEST-South project area. The area of re-analyzed RGS samples is shown in blue, and the approximate area of in-fill sampling is shown in purple.

A variety of digital products accompany this report, allowing visual interrogation of the data using geographic information systems (GIS) or Google Earth. One commodity element (Cu) is provided as an example in this report to illustrate the interpretive work flow and validation process.

Ge¢science BC

Page 4 of 25

Geochemical Catchment Analysis

The two main factors that need to be addressed in the interpretation of stream sediment geochemical data are catchment geology, which controls background geochemistry, and the effect of dilution, which determines whether geochemical anomalies related to mineralization within a particular catchment basin can be detected. Bonham-Carter and Goodfellow (1986) demonstrated that catchment lithology was the main control on observed variation in stream sediment data from the Nahanni region of the Yukon Territory. Other effects such as catchment area, possible adsorption of some elements onto secondary Fe and Mn oxides or onto organic material, and water pH were considered to be minor by comparison. Bonham-Carter et al. (1987) applied a similar approach to stream sediment data from the Cobequid Highlands of Nova Scotia and further concluded that use of the dominant lithology in the catchment basins was not as effective as taking into account the areal extent of all lithologies in the catchment. The effect of catchment area on the interpretation of stream moss matt sediment data in British Columbia was assessed by Sibbick (1994) for an area of northern Vancouver Island using manually estimated catchment areas. Sibbick (1994) noted correlations between catchment area and some elements that were interpreted to reflect increasing stream energy in smaller catchments. It was also noted that less than 10% of known Cu occurrences were found in catchments in the upper 80th percentile of the moss matt sediment Cu data, even though 70% of the sampled catchments contained known occurrences. The poor response of the raw Cu data in this study was attributed to high Cu background values in the Karmutsen Volcanics. Once stream sediment data have been corrected for the effects of catchment geology and size, the data can be interpreted reliably using conventional geochemical exploratory data methods, including multivariate techniques (Carranza and Hale, 1997; Carranza, 2009).

The effects of dilution on stream sediment data have long been recognized, and are described in a mathematical formulation that is sometimes referred to as the productivity of a catchment basin (e.g. Hawkes, 1976). This theoretical calculation involves numerous assumptions, such as equal erosion in all parts of the catchment and *a priori* knowledge of the size and grade of any exposed mineral deposit within the catchment, as well as background values of the elements of interest. Pan and Harris (1990) expanded on this early work to account for the distance downstream between the source of metal in the catchment and the collection point of a series of samples. These approaches were deemed simplifications applicable only to specific areas by Moon (1999), who provided a more involved analysis of stream productivity for high relief areas based on historical Russian research. Critical to these approaches is an estimate of catchment area and an understanding of catchment geology.

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Page 5 of 25

These published case studies indicate the need to account for the effects of dilution from large catchment basins, but generally use productivity calculations to compensate for this effect. Large regional stream sediment datasets commonly involve a wide range of catchment sizes, and it is no coincidence that most elevated raw metal values occur in the smallest catchments where the effects of dilution are minimized. Some of the larger catchments will overlap multiple rock types, complicating some of the productivity approaches described previously, which have tended to assume a single background geochemical population. Furthermore, productivity analysis assumes constant erosion from all areas of the catchment, and in areas of extreme relief this is unlikely to be the case, leading to non-idealised dispersion (Moon, 1999). At the other extreme, in areas of low relief, scavenging effects become more pronounced and the use of residuals from regression analysis of metals against either Fe or Mn may be more relevant than catchment geology (Bonham-Carter *et al.*, 1987). This is often the case when assessing lake sediment data. The assessment of large regional datasets also requires a degree of automation to determine catchment areas and efficient handling of large datasets.

Methodology

We have used a pragmatic approach for the assessment of new geochemical data from the QUEST South project area. This involves an evaluation of geochemical controls on the data through exploratory data analysis (EDA), correcting for any evidence of scavenging of metals by secondary Fe and Mn oxides or organic matter (as inferred from loss on ignition data), and levelling of the data for the dominant lithological unit in each catchment.

Sample Location Validation

The most critical (and time consuming) step in the process involves the correct attribution of samples to the catchment basin from which the sediment was derived (Figure 2). Initial catchments were provided by the British Columbia Geological Survey based on the existing locations for the original RGS data, which had largely been determined on 1:50,000 scale topographic maps, and the locations of the 2009 Geoscience BC samples, which had been located using global positioning satellites (GPS). The latter samples were found to be accurately located on the 1:20,000 scale provincial terrain resource information management (TRIM I) stream network (Cui, 2010). By contrast, a number of the RGS samples were found to lie off the TRIM I stream network and manual adjustment of the sample locations was required. Each sample in the appended data spreadsheet has therefore been tagged with a value based on the degree of confidence in the sample location (Table 1).



Page 6 of 25

Prior to the sample location validation of the 8536 RGS samples, the samples were 'snapped' to the closest stream using a GIS query. Most sample locations were validated using the original 1:50,000 mapsheets onto which the samples had been located following their collection. Where hard copies of maps and sample locations were not available, sample locations were evaluated based on metadata such as stream width or stream order. There are 5 levels of certainty in sample location. The lowest level "-1" is for locations with indefinable catchments, or sample locations that don't have streams within hundreds of metres. No catchments were defined for these samples. The second lowest level, "1", corresponds to sample locations that look reasonable based on stream order or stream width metadata, but still have a high degree of uncertainty because they're located near a fork. In questionable circumstances, the sample locations have been moved downstream of the fork to incorporate both tributaries, which is preferable to attributing the sample to the incorrect basin. Level "2" sample locations are similar to level 1, but have a higher degree of certainty. Level "3" samples were original snaps from the GIS query that appear realistic based on the stream order. Level "4" samples have the highest level of certainty and have been validated against the original survey maps.

Certainty	Description
-1	Uncertain. No definable basin. Use with caution
1	Moderately certain. Samples near forks
I	adjusted to encompass larger basins
2	Certain. Verified against stream order and width
	Very certain. Snapped using GIS query and validated
3	against hard copy maps
4	Completely certain. Validated with hard copy maps

 Table 1. Summary of sample validation certainties.

Catchment basins for the adjusted RGS and new Geoscience BC samples were calculated from the TRIM I heights of land data using the automated process described by Cui *et al.* (2009). The object file of the sample catchments thus produced (Figure 3) was used to query the 1:250,000 bedrock geology of the QUEST South project area (Figure 4) and extract the various proportions of bedrock units within each catchment using a standard query language (SQL) query in a GIS. Although only the dominant bedrock lithology has been used to level the geochemical data in this study, the complete query results have been provided in digital format as part of this report.

Geoscience BC

Page 7 of 25



Figure 2.Locations of individual samples for the QUEST South project area and some known deposits.



Figure 3.Catchments derived for the QUEST South samples from TRIM I heights of land data.





Figure 4.Bedrock geology of the QUEST South project area showing regional trends and structural breaks.

The new geochemical data from Geoscience BC Reports 2010-4 & 2010-13 were used for all elements with the exception of gold. Most new geochemical data were obtained following an aqua regia digestion of a 0.5 g sample with an inductively-coupled plasma (ICP) mass spectrometer (MS) or optical emission spectrometer (OES) instrumental finish. A sub-set of elements for the new in-fill samples reported in Geoscience BC Report 2010-13 was analyzed by instrumental neutron activation analysis (INAA), including Au, but the sample size was not reported. Historical gold analyses from the original RGS analyses were obtained through INAA of samples having an average weight of 23 grams. The original RGS INAA values are generally significantly higher than those obtained by the ICP-MS re-analyses of the same samples (Figure 5). This is particularly evident for the 2009 GBC data. The historical RGS INAA and 2009 GBC INAA data are considered to be more representative than the 2009 GBC ICP-MS data and were the preferred Au values used for interpretation and plotting. In spite of their greater sample mass, the RGS INAA gold data have a root mean squared (RMS) relative standard deviation (RSD) of 51% based on an assessment of duplicate analyses, with the duplicates showing a positive bias. The overall precision of the new gold ICP-MS data from a 0.5 g sample is presumably much worse than this, although no quality control data were provided in Geoscience Reports 2010-4 & 2010-13 to allow an assessment of data quality. Where RGS INAA duplicate data were available, the average of the two values was used for plotting and interpretive purposes.



Page 9 of 25



Figure 5.Comparison of historical RGS INAA Au data and GBC ICP-MS Au data from the sample samples. A line of equal composition is included for reference.

Exploratory Data Analysis

Exploratory data analysis was undertaken using ioGAS geochemical assessment software to examine multivariate relationships within the ICP data and to determine if inter-element associations suggested possible scavenging of metals onto secondary Fe and Mn oxides, or onto organic matter. The elements Co, Cu, Ni, Cr, Sc show statistically significant correlations ($r^2 > 0.4$; Spearman Rank or log_{10} transformed Pearson Product Moment correlations) with Fe, as well as Mn. The elements Zn, Sb, Ba, Ag, Mo and As show similar correlations with Mn. Accordingly, these elements were regressed against the relevant independent (explanatory) variables after log_{10} transformations using robust methods to remove the influence of statistical outliers. Mercury shows a statistically significant correlation with loss on ignition (LOI) data, which can be used to infer the level of organic material within the samples, and this is a common association. Unfortunately, LOI data are not available for all samples and so regression analysis of all samples using LOI as the independent variable could not be undertaken. Instead, Hg was regressed against Mn, with which it also shows a statistically significant positive correlation.



Page 10 of 25

Data from new samples collected in 2009 by GBC were compared to re-assayed RGS samples from the same geographic area to test for systematic differences in data from the two different laboratories used for analyses. Although both laboratories used aqua regia, there are many subtle variants of this acid digestion that can introduce a systematic shift in data from separate laboratories. In particular, the elements Ag, Hg, Mn, Na, Pb, S, Te and Tl appear to be significantly different in data from the same approximate geographic region. In all cases, with the exception of Hg and Tl, the data obtained by GBC for the new samples collected in 2009 give higher median values than the re-analyzed RGS samples. The Te data for the 2009 Geoscience BC samples are significantly different, and of lower quality in terms of data precision, than the RGS re-assay data. Therefore, in addition to raw element gridded images, data levelled by source laboratory has also been provided for these elements. Z-score levelling (sample value mean/standard deviation) following \log_{10} transformation has been used where appropriate, and median levelling (value/group median) used otherwise. In order to account for the possibility of a systematic shift in data generated by individual laboratories without explicitly levelling the data for this effect, regression analysis was undertaken independently for the two data sets. However, a clustering of the samples collected in 2009 around areas such as Highland Valley and an affiliation of some of the elements affected with the a potential pathfinder suite associated with Cu-Mo porphyry-style mineralization suggests that some of the bias in the data may be real and related to the presence of mineralization within the catchments sampled.

Raw geochemical data were also levelled against the dominant bedrock lithology within the catchment. Some merging of geochemically similar lithological units was required in order to maintain a minimum population of 10 samples in each lithological group. The samples were Z-score levelled following a log₁₀ transformation of the data. Robust residuals were also levelled by dominant catchment lithology. It should be noted that high levelled values are not necessarily indicative of mineralization within a catchment area. They could also represent errors in the bedrock geology as mapped, the presence of a minor but geochemically enriched bedrock unit (e.g. black shale) near the sample site, or reflect unequal erosion within the catchment region whereby a geochemically distinct lithology contributes a disproportionate amount of sediment to the catchment.

As pointed out by Bonham-Carter *et al.* (1987), using the dominant catchment lithology to infer background geochemical levels is likely inferior to calculating catchment productivities based on a complete assessment of catchment geology. However, the latter approach is computationally more involved. Background values for each lithological type must be estimated from those catchments having

QUEST-South Geochemistry



Page 11 of 25

predominantly a single bedrock lithology, and these values used to calculate a weighted average background value for the catchment based catchment geology. Alternatively, background values could be estimated from median values for each element in those catchments for which a particular lithological unit is the dominant bedrock in the catchments. Equal erosion, and thus equal contribution from each bedrock unit in the catchment, is assumed.

Data Presentation

The effects of regression analysis and levelling for dominant bedrock lithology are summarized in Figure 6 for Cu. Z-score levelling was used in order to maintain the overall distribution of data from individual groups, including near (circles) and far (triangles) outliers in the data. There is clearly significant variation in the raw geochemical data associated with different dominant lithological units in each catchment. These variations are somewhat moderated when robust residuals are plotted instead of raw data, and are effectively dampened by the levelling process. Gridded images created using data levelled by dominant catchment lithology therefore emphasize outliers in each group, rather than the geochemical variations associated with variable catchment geology. However, levelling can also dampen lithological variations that may be of interest, such as elevated Cu in feldspar porphyritic intrusive rocks of the QUEST South region (Figure 6), and therefore may subdue the geochemical response of mineralization associated with specific rock types. The use of all images (raw, residuals and levelled) is recommended for exploration targeting purposes.

A comparison of gridded geochemical images for Cu in Figure 7 is used to illustrate the effects of the various data levelling techniques employed in the course of this study. These figures are gridded unequally on a percentile basis, with the red, pink and white areas indicative of the upper 95th, 98th and 99th percentiles, respectively. The gridded raw Cu data correlate with many known Cu deposits and occurrences (Figure 7a), although there are also numerous instances where upper percentile data show no association with known mineralization, and therefore may present potential exploration targets. The response for a number of these areas is either dampened or removed where residuals against Fe have been calculated (Figure 7b). Levelling the Cu data for the dominant catchment bedrock unit also serves to dampen the response in those areas where elevated Cu is present in the absence of known Cu mineralization (Figure 7c). The two adjustments to the data are combined in Figure 7d, where Cu residuals have been Z-score levelled by dominant catchment geology. In all cases, the clear response shown by the raw Cu data associated with major Cu deposits is maintained. The main effect of regression



Page 12 of 25

analysis and levelling is to enhance subtle effects in the grids, such as geochemical trends, rather than to radically alter the obvious geochemical anomalies.



Figure 6. Box and whisker plots illustrating the effects of regression analysis and Z-score levelling for catchment bedrock geology on the distributions of stream sediment geochemical data classified on the basis of dominant catchment rock type.

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As a final caveat on the use of the gridded images, they are particularly useful for detecting regional trends, but their use when viewed in detail is limited or even misleading. Follow-up investigations of individual samples and their catchments should make use of thematic map products so that the actual catchments from which the geochemical responses were obtained are identified.

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Figure 7a. Gridded raw Cu data from the QUEST South project area. The image is overlain by known Cu deposits, occurrences and regional structures.



Figure 7b. Gridded robust Cu residuals following regression against Fe data from the QUEST South project area. The image is overlain by known Cu deposits, occurrences and regional structures.

QUEST-South Geochemistry

Geoscience BC



Figure 7c. Gridded Z-score log₁₀ transformed, levelled by simplified rock type, Cu from the QUEST South project area. The image is overlain by known Cu deposits, occurrences and regional structural geology.



Figure 7d. Gridded robust Cu residuals, Z-score levelled by simplified rock type, from the QUEST South project area. The image is overlain by known Cu deposits, occurrences and regional structural geology.

QUEST-South Geochemistry

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Additive Pathfinder Indices

Robust residuals and levelled data from individual elements can be combined to create a series of additive pathfinder indices that may be more instructive for particular mineral deposit types (Figures 8a-8d). Gold, where used in these indices, has been Z-score levelled by levelled by rock type to re-scale the data so that it is equally weighted with the other possible pathfinder elements. Robust residuals have been used for those elements that show a statistically significant positive correlation with either Fe or Mn. Examples of additive index gridded images that have been produced for this report include Au+As+Sb (orogenic Au, Figure 8a), Au+Ag+Hg (epithermal Au, Figure 8b), Cu+Pb+Zn (base metals, Figure 8c) and Cu+Au+Mo (porphyry-style, Figure 8d). Robust residuals and levelled data are provided with the raw geochemical data in this report, and the reader is encouraged to compile their own additive indices for the appropriate pathfinder element suite. The use of Au in these indices is subject to the precision issues previously discussed, but the effects are moderated by the use of associated pathfinder elements. Of these four deposit styles, the additive index for orogenic gold is by far the most coincident with known mineral occurrences.

RGB Analysis

An alternative mode of presentation is to rank three elements together where each represents an anomalous geochemical population in their own right (Figure 9). Rather than using strict percentile values, the relevant thresholds used for the RGB analysis have been based on the analysis of probability plots of robust residuals and levelled data. The analysis allows anomalies to be ranked in terms of increasing association to a predicted pathfinder element suite using both colour and symbol size. The thematic maps thus generated have been exported as KMZ files that can be opened in Google Earth. RGB thematic maps have been produced for the pathfinder element suites described in the previous paragraph.





Figure 8a. Gridded image of orogenic gold pathfinders, using an additive index of levelled and residual Au, As, and Sb.



Figure 8b. Gridded image of epithermal gold pathfinders, using an additive index of levelled and residual Au, Ag, and Hg.

QUEST-South Geochemistry





Figure 8c. Gridded image of base metal deposit pathfinders, using an additive index of levelled and residual Cu, Pb, and Zn.



Figure 8d. Gridded image of Cu-Au porphyry-style pathfinders, using an additive index of levelled and residual Cu, Au, and Mo.

QUEST-South Geochemistry

Ge⇔science BC

Page 19 of 25



Figure 9. RGB thematic for elevated raw Au above 65 ppb, elevated Z-score levelled robust Sb residuals, and elevated Z-score levelled robust As residuals for the QUEST South project area. Samples below the RGB thresholds have been omitted for visual clarity.

Multivariate Analysis

Multivariate analysis has been used as a way to query the dataset in order to see what elemental groupings exist. Robust principal component analysis (PCA) was undertaken on a subset of the data containing all likely commodity and pathfinder elements following log₁₀ transformation, as well as major elements likely to control the distribution of the trace elements. The first 5 principal components, comprising 75% of the variability in the data, are dominated by complex relationships likely controlled by catchment geology. For example, PC2 is loaded by Co, Ni, Cr, Fe, Mg and Na, indicating a mafic to ultramafic rock association. The higher principal components, from PC6 to PC9, collectively comprise approximately 12% of the variability in the data. PC6 reflects a Hg-W-Sb-As-Cu-Ni association. PC7 (Figure 10) is dominated by Ag-Pb-Cu-Ni-Bi. PC8 represents a K-Cu-Mo-As-Zn association, and PC9 reflects a Hg-Mo-Au-Ni-K grouping.





Figure 10. Gridded image of PCR7 (Ag-Pb-Cu-Ni-Bi) with known Pb and Ag occurrences.

Optimum Catchment Area

Once the catchment areas are known for the individual samples, it's possible to empirically evaluate the effects of dilution in the catchment basins (Figure 11). For most metals, the catchment area at which regional background values are reached varies from approximately 300 to 500 km², depending on the element. For example, regional Zn background values do not exceed 100 ppm, and this value is reached for the majority of catchments within about 250 km². A similar catchment area is suggested for a maximum regional background for Au of 10 ppb. Samples with metal values significantly higher than those expected for their catchment areas following correction for possible scavenging effects and/or catchment bedrock lithology represent anomalous samples worthy of further investigation. They either represent catchment areas with metal values significantly above regional background, or perhaps samples for which the wrong catchment may have been assigned, although reasonable steps have been undertaken to minimize that possibility in this data set. This graphical approach to catchment "productivity" makes none of the assumptions inherent in the direct application of the theoretical calculation. The data can be also be used to constrain a maximum catchment area for follow-up or in-fill sampling, which in this instance would be 250 km².



Page 21 of 25

12-Apr-11



Figure 11. Contoured scatter plot showing the relationship between raw metals and catchment area for the QUEST South project area. Catchments larger than 5,000 km² have been omitted from the plots.

Given the previous discussion on maximum catchment area for effective sampling, it will be clear that a number of stream sediment samples have sampled catchments greater than 250 km², assuming that the sample locations used for catchment generation are correct. Coding of catchments that are greater than this area (Figure 12) identifies those areas that have potentially been under sampled and would benefit from in-fill sampling at a higher density. These areas represent exploration opportunities in an area that may have been considered adequately sampled by the previous RGS program.





Figure 12. Catchment basins greater than 250 km² are shaded and represent areas that may not have been effectively sampled by the original RGS surveys.

Conclusions

Catchment basins have been determined by the Geological Survey of British Columbia for 9312 reassayed RGS and new stream sediment samples. The dominant bedrock lithology for each catchment has been determined and used to level the stream sediment geochemical data for the effects of variable background lithology. In addition, EDA has indicated that several potential pathfinder and commodity elements show statistically significant positive correlations with Fe and/or Mn, suggesting that scavenging of metals by secondary Fe and/or Mn oxide minerals may have occurred. This effect has been corrected through robust regression analysis and the use of residuals. Regression analysis has been undertaken separately for data obtained from two different laboratories in order to account for possible systematic biases in the data. The residuals and levelled data have been used to produce a series of single and multi-element gridded images in Geotiff format, as well as a series of RGB thematic maps in Google Earth format. These products do not differ dramatically from the raw geochemical data, but provide enhancement of subtle geochemical features in the data that would otherwise not be apparent. Assessment of these subtle features, when coupled with an understanding of mineral deposit pathfinder associations and regional controls on mineralization, will be of use in future mineral exploration programs.



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QUEST-South Geochemistry



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