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Notes

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ABSTRACT: Geochemical data are generally derived from government and industry geochemical surveys that cover areas at various spatial resolutions. These survey data are difficult to assemble and integrate due to their heterogeneous mixture of media, size fractions, methods of digestion and analytical instrumentation. These assembled sets of data often contain thousands of observations with as many as 50 or more elements. Although the assembly of these data is a challenge, the resulting integrated datasets provide an opportunity to discover a wide range of geochemical processes that are associated with underlying geology, alteration, landscape modification, weathering and mineralization. The use of data analysis and statistical visualization methods, combined with geographical information systems, provides an effective environment for process identification and pattern discovery in these large sets of data.

Modern methods of evaluating data for associations, structures and patterns are grouped under the term 'data mining'. Mining data includes the application of multivariate data analysis and statistical techniques, combined with geographical information systems, and can significantly assist the task of data interpretation and subsequent model building. Geochemical data require special handling when measures of association are required. Because of its compositional nature logratios are required to eliminate the effects of closure on geochemical data. Exploratory multivariate methods include: scatterplot matrices (SPLOM), adjusting for censored and missing data, detecting atypical observations, computing robust means, correlations and covariances, principal component analysis, cluster analysis and knowledge based indices of association. Modelled multivariate methods include discriminant analysis, analysis of variance, classification and regression trees neural networks and related techniques. Many of these topics are covered with examples to demonstrate their application.

KEYWORDS: *geochemistry, data analysis, visualization, statistical methods, data interpretation, review*

A review of contributions to the Exploration 1977, 1987 and 1997 conferences held in Toronto in the field of exploration geochemistry and the interpretation of regional geochemical survey data provides a perspective and appreciation of the very powerful tools that geoscientists now have at their disposal. Boyle (1979) described the first part of the twentieth century when rapid advancements were made in the recognition of primary and secondary dispersion haloes: development of accurate and rapid analytical methods (e.g. the development of atomic absorption spectroscopy, fluorimetry, chromatography, neutron activation analysis, mass spectrometry); improvements in sampling technologies; radiometric methods, airborne geochemical sampling methods; improvements in field techniques and access (helicopters); heavy minerals in glacial media; and developments in statistical and computer techniques. At that time, Boyle also pointed out that further research was required to understand the trace and major element chemistry of rocks and their geochemical relationship to metallogenic belts. Boyle also noted that future research should focus on the identification of mineral deposits at depth, and for countries such as Canada, the evaluation of basal till geochemistry is an effective means of exploration for metallic mineral deposits. The role of government surveys in the collection of various geological media and subsequent geochemical analysis was considered paramount for a successful mineral exploration strategy for any country. Boyle discussed the term 'vectors' as a means to identify mineral deposits through the evaluation of patterns and trends in geochemical data in both two and three dimensions.

At the time of Exploration 77, the use of geochemical data in glacial terrains, (Bølviken & Gleeson 1979), non-glaciated terrains (Bradshaw & Thomson 1979), lithogeochemistry (Govett & Nichol 1979), biogeochemistry (Brooks 1979; Cannon 1979), stream sediment geochemistry (Meyer *et al.* 1979), lake sediments (Coker *et al.* 1979) and hydrogeochemistry were well advanced. The fundamentals of these developments are still applicable today. There have been refinements in methods of extraction (digestion methods and selective

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leaches), improvements in detection limits and better understanding of the sedimentary environments of stream, lake, glacial and weathered environments. Howarth & Martin (1979) provided the basics of evaluating geochemical data, the principles of which are still in use today. The term 'integration' was already in use in the 1970s when it was realized that several types of geoscience data could be merged using computer-based methods (Coope & Davidson 1979).

The Exploration '87 meeting contained similar discussions along the lines of weathered terrains (Butt 1989; Mazzucchelli 1989; Smith 1989), glaciated terrains (Coker & DiLabio 1989; Shaw 1989), stream sediments (Plant *et al.* 1989), lake sediments (Hornbrook 1989), biogechemistry (Dunn 1989), and bedrock geochemistry (Govett 1989). In addition, the role of computers, databases and computer-based methods for use in mineral exploration were distinct contributions to the meeting (Garrett 1989*a*; Harman *et al.* 1989; Holroyd 1989) and expert systems were introduced as a means for decision-making in exploration (Campbell 1989; Martin 1989). Exploration '87 also contained more results on the benefits of integrated exploration strategies.

Exploration '97 covered much of the same material of advances in geochemical exploration methods for the geochemistry of glaciated terrains (Klassen 1997; McClenaghan *et al.* 1997), the geochemistry of deeply weathered terrains (Mazzucchelli 1997; Smith *et al.* 1997), geochemistry of stream sediments (Fletcher 1997), lake sediment geochemistry (Friske 1997; Davenport *et al.* 1997*a*), lithogeochemistry (Franklin 1997; Harris *et al.* 1997), plus developments in extraction techniques for the enhancements of geochemical responses (Bloom 1997; Hall 1997; Smee 1997). Closs (1997) emphasized that careful sample design and objectives are the fundamental tenets of exploration geochemistry, which had not changed in the previous 30 years. Integrated exploration information management was a major focus at the Exploration '97 conference with significant contributions by Bonham-Carter (1997), Davenport *et al.* (1997*b*), de Kemp & Desnoyers (1997) and Harris *et al.* (1997) along with the early developments on the use of the world wide web (internet) by Cox (1997).

Prior to the arrival of Geographic Information Systems (GIS) and desktop statistical computing packages, exploration geochemistry was limited in scope in terms of extensive data analysis. Textbooks such as those by Hawkes & Webb (1962), Rose *et al.* (1979) and Levinson (1980) provided the foundation for exploration geochemistry strategies and defined the principles for planning, executing and interpreting geochemical surveys. These texts were written before the development of GIS or easily accessible statistical packages. As a result, they offered limited treatment for a statistical analysis of geochemical survey data. In the late 1980s, GIS began to play an increasingly important role in the display and management of spatially referenced data (e.g. geochemical data). These systems required large computers and specialists in the management and maintenance of the software. GIS have evolved into 'Desktop Mapping' systems that allow users of personal computers to display, query, manage, and to a limited extent analyse spatially referenced data.

Geochemical surveys are an important part of geoscience investigations in both mineral exploration and environmental monitoring. The International Geological Correlation Program (IGCP Project 259 (Darnley *et al.* 1995) summarized the value of geochemical surveys for both exploration and global change monitoring. This report contains recommendations for sampling strategies, data management, analytical methods and numerous other topics for the development of a global network of geochemical knowledge. A soil or lake sediment survey can consist of collecting several thousand specimens and be analysed for at least 50 elements. Analysing and interpreting these large sets of data can be a challenge. Data can be categorical (discrete numeric or non-numeric) or continuous in nature. To extract the maximum amount of information from these data, various multivariate data analysis techniques are available. In many cases, these techniques reduce these large datasets into a few simple diagrams that outline the principal geochemical trends and assist with interpretation. The trends that are identified may include variation associated with underlying lithologies, zones of alteration, and in special cases, zones of potentially economic mineralization. Areas of mineralization are typically small in geographic extent and less likely to be 'sampled' in the course of regional geochemical sampling survey. Thus, they can be considered as rare events relative to the regional geochemical signatures within a study area and they will commonly be under-represented within a population. This means that they may be observed as atypical or masked by the main mass of the population.

The term 'sample' in statistical literature, usually refers to a selection of observations from a population. In the lexicon of geoscientists, specimens of soil, rocks, stream sediments and other such media, are generally called 'samples'. This has been a source of confusion between the geoscience and the statistical communities. Within this contribution, specimens (i.e. the geochemist's samples) that have been collected in the field are referred to as 'specimens' and the data derived from them as 'observations'. Elements are the geochemical entities that become variables in the application of statistics. The terms 'variable' and 'element' are used interchangeably in this contribution. Specimen collection strategies are an important part of any geochemical survey programme. Garrett (1983, Chapter 4) provides a useful discussion on various approaches for sampling media for geochemical surveys.

The evaluation and interpretation of geochemical data rely on understanding the nature of the material that has been sampled. Different materials require a variety of methods and techniques of data analysis for the interpretation of geochemical results. In the case of surficial sedimentary materials (glacial till, lake and stream sediments), different size fractions of specimens can reflect different geological processes. The choice of size fraction can have a profound influence on the interpretation of the geochemistry of an area. In any geochemical survey the material for study should be carefully collected and classified in order to provide any clues about the underlying geochemical processes.

Quality control is an essential part of assessing geochemical data. All data should be initially examined for analytical reliability and screened for the identification of suspect analyses. Typically, this is done using exploratory data analysis (EDA) methods. Issues of quality control, analytical accuracy and precision are beyond the scope of this contribution; however, it is briefly discussed in the section, 'Special Problems'.

Five sets of data have been used in this contribution.

1. *Lithogeochemical data from Ben Nevis township, Ontario, Canada* (*Plate 1*). Rock specimens were collected as part of a study to examine the nature of alteration and associated mineralization in a sequence of volcanic rocks (Grunsky 1986*a*, *b*). Two significant Zn–Ag–Cu–Au occurrences have been investigated in this area: the Canagau Mines deposit and the Croxall property (Grunsky 1986*a*). The results of a detailed lithogeochemical sampling programme outlined a zone of extensive carbonatization associated with the Canagau Mines deposit. The alteration consists of a large north–south trending zone of carbonate alteration with a central zone of

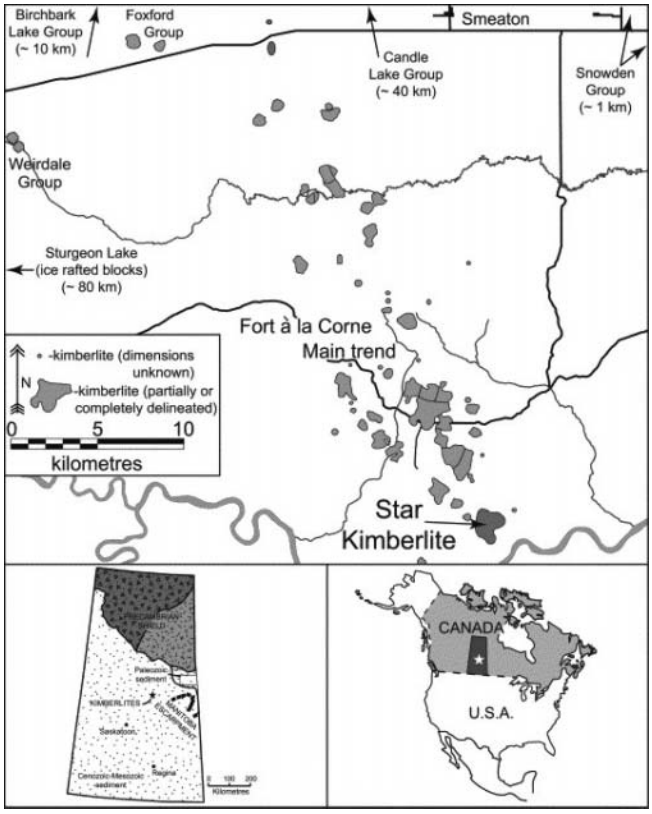


Fig. 1. Location map of the Fort à la Corne kimberlite field, Saskatchewan, Canada.

silica enrichment with gold and copper sulphide mineralization. A lesser zone of carbonatization is associated with the Croxall property. Small isolated zones of sulphide mineralization occur throughout the area. The specimens were not collected over a regular grid but were collected wherever rock outcrops could be located in the field. The geology of the area and the specimen locations are shown in Plate 1. Lithogeochemical sampling was carried out over the area in 1969, 1972 and 1979–1981. A total of 825 specimens were analysed for SiO_2, Al_2O_3, Fe_2O_3, FeO, MgO, CaO, Na_2O, K_2O, TiO_2, P_2O_5, MnO, CO_2, S, H_2O^+, H_2O^-, Ag, As, Au, Ba, Be, Bi, Cl, Co, Cr, Cu, F, Ga, Li, Ni, Pb, Zn, B, Mo, Sc, Sn, Sr, V, Y, U and Zr. Initially, the major element oxides were assessed using a multivariate procedure known as 'correspondence analysis' that is documented in Grunsky (1986*a*). Details on the geology, sampling methodology and mineral occurrence descriptions can be found in Grunsky (1986*b*). A regional picture of the alteration and prospectivity for volcanogenic massive sulphide deposits can be found in Hannington *et al.* (2003).

2. *Lake sediment survey data from the Batchawana district, Ontario, Canada (Plate 2).* This set of survey data, consisting of 3047 lakes sediment specimens collected between 1989–1995, from a series of lakes that overlie a Precambrian volcanic-sedimentary sequence that has been intruded by granitic rocks (Grunsky 1991). The lake sediments in the area are derived from the underlying bedrock (shown in the legend), glacial overburden and organic matter (not shown). Glacial till, outwash sand, lacustrine deposits and recent re-worked glacial deposits blanket the area in varying thickness. Bedrock exposure is less than 5% of the area with most of the glacial overburden being less than 3 m.
3. *Data from the island of Sumatra, Indonesia.* This dataset, from a soil survey over a Cu–Au prospect on the island of Sumatra, Indonesia, provides an example of how multivariate data analysis and digital elevation data can be used to isolate geochemical responses related to different processes. A geochemical survey was carried out on a grid of lines 100 m apart with sampling sites every 25 m. The geology is poorly understood because of extensive weathering in the tropical climate. The mineralization of Cu and Au occurs in breccia zones that are associated with a felsic intrusion and appear to be structurally controlled as en echelon fractures that parallel the great Sumatra fault. Plate 3 shows the generalized geology for the area.
4. *The Campo Morado mining camp in the Guerrero state of Mexico.* This camp hosts seven precious-metal-bearing volcanogenic massive sulphide deposits in the complexly folded and faulted Guerrero terrain (Oliver *et al.* 1996; Rebagliati 1999), shown in Plate 4. A total of 29 221 samples were collected over a soil grid comprising 25 m sample spacing along lines and each line was 100 m apart. The field samples were analysed for Al, Fe, Ca, K, Mg, Na, Ti, Au, Ag, As, Ba, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, P, Pb, Sc, Sr, V, W and Zn using *aqua regia* digestion and ICP-ES. A digital elevation model (DEM) was created at 25 m resolution. Plate 4 shows the location of each sample point and is coloured according to the lithology over which the sample was collected. The high density of sampling yields a detailed picture of the lithologies of the area as shown in the figure. Principal component analysis (PCA) was carried out on the data and revealed several significant patterns related to lithological variation and mineralization.
5. *Kimberlite bodies from Fort à la Corne Saskatchewan (Fig. 1).* Five kimberlite phases from the Fort à la Corne area of Saskatchewan have been analysed for major and trace element geochemistry. These five phases are shown to be statistically distinct and can be used to form the basis of a classification scheme for scoring unknown samples (Grunsky & Kjarsgaard 2008). Because of confidentiality requirements, geographic coordinates are not presented with these results.

GEOCHEMICAL DATA MINING

Data mining involves the use of automatic and knowledge-based procedures for the recognition of patterns that can be attributed to known processes (i.e. crystal fractionation, hydrothermal alteration, weathering). Common forms of data mining involve supervised and unsupervised pattern recognition. Unsupervised data mining includes techniques such as cluster analysis, principal component analysis, exploratory data analysis, multivariate ranking of data, neural networks and empirical indices. These methods vary from automatic, semi-automatic, to manual in the degree of pattern delineation. The use of a fully automatic method does not guarantee a result that necessarily represents the best view or meaningful structure in the data. Caution must be applied in using such techniques. Supervised methods include discriminant analysis, canonical variate analysis, model-based clustering, neural networks, support vector machines and cell automata. All require *a priori* assumptions and/or 'target' and 'background' definitions to which unknown data can be classified. Typically, target populations represent sets of geochemical data that define mineral exploration targets.

Visualization of geochemical data

Visualization is one of the most effective ways of evaluating data. The human eye is more adept at recognizing patterns from pictures than with tables of numbers. Geochemists need to

evaluate data comparatively in both the spatial domain (geographic location) and the variable (element/oxide) domain. When a single element's data are being evaluated, simple plots such as probability plots (Sinclair 1976; Stanley & Sinclair 1987, 1989; Stanley 1987), histograms, or box plots can be used. However, there are many other ways to evaluate data graphically. Many of these methods have been outlined by Cleveland (1993). Garrett (1988) developed a data analysis, statistics and visualization system, IDEAS, that provides a multitude of methods that are useful to the exploration geochemist. This package was recently replaced by another package, 'rgr' (Garrett & Chen 2007) and is available from www.r-project.org. Reimann *et al.* (2008) have published a book that provides methods for evaluating geochemical data in an environmental context using R.

Even the field of statistical evaluation of data has changed significantly in the past 10 years. This is exemplified by texts that combine extensive visualization techniques (Sarkar 2008) together with modern statistical methods (Venables & Ripley 2002).

This contribution has made extensive use of the data analysis and statistical analysis software package, R (R-Development Core Team 2008), which provides a number of powerful tools for manipulating and visualizing data. Most of the statistical graphics herein have been created using R. The application of this environment for geoscience applications is described by Grunsky (2002*a*).

Geographical information systems

GIS represent digital visualization of spatially-based data on a map. GIS require a spatial definition of the data plus attribute tables that contain information relevant to the specified geographic locations and the representation of geochemical data. Examples of this have been presented by Mellinger *et al.* (1984), Gaál (1988), Kuosmanen (1988), Bonham-Carter (1989*a*, *b*), George & Bonham-Carter (1989), Hausberger (1989) and Mellinger (1989). In particular, GIS facilitates the organized storage and management of spatially-based data that are linked to a number of other features or other geo-referenced data sets. Bonham-Carter (1994) has written a monograph of geoscience applications using GIS and Harris (2006*a*) has edited a volume on GIS applications in the Earth sciences covering a wide range of topics in which geochemistry is covered by Cheng (2006), Grunsky (2006), Harris (2006*b*) and Wilkinson *et al.* (2006).

As geoscience information and data become available in ever-increasing volumes, exploration programmes and government research programmes involve significant amounts of data compilation. The compiled datasets are subsequently placed into GIS and integrated with other geoscience information. Recent developments in the use of GIS together with data compilation programmes have been discussed in Wilkinson *et al.* (1999) and Harris *et al.* (1997, 1999, 2000) and a book with a chapter on the evaluation of geochemical data using GIS (Harris 2006*a*, Chapters 12–16).

Depending on the nature of the geochemical data (stream sediment, soil, lake sediment, or lithogeochemical), various types of analysis can be performed that are dependent on the type of associated data present. Point, polygon (vector) and raster (regular array cells) features can be overlain, merged and analysed through the associated map merging and database querying tools. Raster image grid cells can be considered as points provided there is an associated attribute record of data with each grid cell.

Desktop mapping systems have evolved to the point that they are cheaper and less complex, are easier to use and offer an effective way for the geochemist to evaluate data. Thus, the goals of the geochemist can be achieved faster and at less cost. As digitally based map and attribute data are being created continually, there has been an increasing demand to view and assess these data without the use of complex GIS. In its simplest form, a desktop mapping system has significant advantages in exploration geochemistry. Geochemical data can be loaded and visualized in both the geochemical space and the geographical space very quickly. Geochemical data can also be processed using a number of statistical or other data analysis techniques from which the results can also be loaded into a desktop mapping system. The permutations and combinations of data layer manipulation provide a wide variety of ways of examining and interpreting data.

Image processing

When the sampling density of geochemical data is adequate, it is desirable to produce maps that represent smoothed gridded data and coloured/shaded surfaces. Smoothed, gridded data can be considered a raster image. Image analysis is primarily used for presentation purposes to enhance the results of an analysis or to show variation within data. Image analysis manipulates integer-scaled raster data using a number of matrix-based methods and after the use of additional integer-scaling procedures represents the resulting transformed data on various graphical output devices using colour (e.g. intensity, hue, saturation, RGB, CMYK). Richards & Jia (1999) provide an introduction to image processing methods. Carr (1994) provides an introduction to image processing in geological applications and Gupta (1991) and Vincent (1997) provide comprehensive reviews of remote sensing applications in geology. Rencz (1999) contains a collection of papers covering the topic of remote sensing in the Earth sciences and Pieters & Englert (1993) covers the topic of remote geochemical analysis through the evaluation of satellite spectroscopy.

Exploratory data analysis (EDA)

Exploratory data analysis is concerned with analysing geochemical data for the purpose of detecting trends or structures in the data. These features can provide insight into the geochemical/geological processes from which models can be constructed. Exploratory methods of data analysis include the evaluation of the marginal (individual) distributions of the data by numerical and graphical methods. These include the use of summary tables (minimum, maximum, mean, median, standard deviation, 1st and 3rd quartiles), measures of correlation, covariance and skewness. Graphical methods include histograms, probability (quantile–quantile) plots, box plots, density plots and ScatterPLOt Matrices (SPLOM). More sophisticated data visualization can be carried out using packages such as the 'lattice' library that is available in R (Sarkar 2008). The spatial presentation of data summaries can be incorporated into a GIS using features such as bubble and symbol plots, and interpolated grids.

Multivariate methods include the use of PCA, cluster analysis, Mahalanobis distance plots, empirical indices and various measures of spatial association.

Target and background populations

In an exploration programme, geochemical background represents a population of observations that reflect unmineralized ground. Background may be a mixture of several populations (gravel–sand–clay or granitoid–volcanic–sedimentary lithologies). The separation of the background population into similar

subsets that represent homogeneous multivariate normal populations is important and forms the basis of the modelled approach of geochemical data analysis. This can be achieved using exploratory methods such as PCA, methods of spatial analysis, Mahalanobis distance plots and cluster analysis.

A group of specimens that represent an entity under investigation (features of geochemical alteration or mineralization) is termed the 'sample' population, from which inferences will be made about the 'target' population that cannot be sampled in its entirety. These populations are derived from specimens collected from orientation studies over known mineral deposits or areas of specific interest.

Sample populations, whether representing background or other populations, represent training sets with unique characteristics. These training sets are generally distinct from one another through their statistical properties, although it is common for training sets to overlap. Unknown specimens can be tested against these populations to determine if they have similar characteristics. Probability-based methods can determine if the unknown specimen belongs to none, one or more of the populations.

A case study is presented where distinctions between kimberlites from the Fort à la Corne area, Saskatchewan have been statistically determined based on their multi-element signatures.

Special problems

Problems that commonly occur in geochemical data include:

- many elements have a 'censored' distribution, meaning that values at less than the detection limit can only be reported as being less than that limit;
- the distribution of the data is not normal;
- the data have missing values. That is, not every specimen has been analysed for the same number of elements. Often, missing values are reported as zero, which is not the same as a specimen having a zero amount of an element. This can create complications in statistical applications;
- combining groups of data that show distinctive differences between elements where none is expected. This may be the result of different limits of detection, instrumentation or poor Quality Assurance/Quality Control (QA/QC) procedures. Levelling of the groups is required;
- the constant sum problem for compositional data.

These problems create difficulties when applying mathematical or statistical procedures to the data. Statistical procedures have been devised to deal with all of these problems. In the case of varying detection limits, the data require separation into the original groups so that appropriate adjustments can be applied to the groups of data.

To overcome the problems of censored distributions, procedures have been developed to estimate replacement values for the purposes of statistical calculations. When data have missing values, several procedures can be applied to impute replacement values that have complete analyses. This will be discussed in more detail further on in the text.

Plate 5 summarizes the problems of censoring, non-normality and the discrete differences in the data due to analytical resolution. The image is a shaded relief map derived from the density of observations of As v. Au. The 'valleys' represent limits in data resolution near the lower limit of detection for Au. The actual limit of detection appears as a 'wall' at the zero end of the Au axis. In contrast, As displays a continuous range of values without the same resolution or detection limit problems exhibited by Au.

Standard numerical and statistical methods have been developed for data analysis where the values being considered add to a constant sum (e.g. whole rock analyses summing to 100%). This is discussed in more detail below.

Quality assurance and quality control of geochemical data require that rigorous procedures be established prior to the collection and subsequent analysis of geochemical data. This includes the inclusion of certified reference standards, randomization of samples and the application of statistical methods for testing the analytical results. Historical accounts of 'Thompson and Howarth' plots for analytical precision studies can be found in Thompson & Howarth (1973, 1976*a*, *b*, 1978). Additional discussion on the subject was most recently covered by Stanley (2003, 2006) and Garrett & Grunsky (2003).

Compositional data

Geochemical data are reported as proportions (weight %, parts per million, etc.) For a given observation compositional proportions (i.e. weight %) always sum to a constant (100%). As a result, as some measures increase, others are 'forced' to decrease to keep the sum constant. Because compositional data occur only in the real positive number space, the calculation of statistical measures, such as correlation and covariance, can be misleading and result in incorrect assessment of correlation or other measures of association. It is dangerous to make the assumption that closure has no effect on the outcome of any statistical measure. Raw compositional data is useful for observing stoichiometric trends in data (e.g. Grunsky & Kjarsgaard 2008); however, any type of regression or procedure that requires statistical measures necessitates the use of logratios which are described below.

Aitchison (1986) developed a methodology for data analysis and statistical inference of compositional data using logratio transformations. These transformations project the compositional data into the entire (positive and negative) real number space, which allows standard statistical procedures to be applied. These methods are gaining popularity and examples of application to geochemical data are given by Aitchison (1990), Grunsky *et al.* (1992) and Buccianti *et al.* (2006). The approach has also been extended into spatial data processing that is commonly used in ore reserve estimation (Pawlowsky 1989). Recent work by Barcelo *et al.* (1995, 1996, 1997), Martin-Fernandez *et al.* (1998, 2000) Pawlowsky-Glahn & Buccianti (2002) and von Eynatten *et al.* (2002, 2003) document methods and issues around the treatment of compositional data. Aitchison (1997) provides a very readable account of compositional data issues. Appendix 1 provides a basic description of the use of logratios. Buccianti *et al.* (2006) provide the most recent developments in the field of compositional data analysis. A package for compositional data analysis (van den Boogaart & Tolosana-Delgado 2008) known as '*compositions*' provides a set of tools for evaluating compositional data using the R statistical package (www.r-project.org).

Most geochemical survey data comprise trace element measurements that are reported as parts per million (ppm). The reporting in ppm constitutes the potential for closure, the trace element concentrations may interfere with each other particularly when one or more of the elements of interest is close to zero. The application of a centred logratio transformation (clr) will provide more reliable and statistically defensible results than the use of raw data. The use of the isometric logratio (ilr) (Egozcue *et al.* 2003), where balances between the elements are constructed, provides orthonormal basis in the compositional data space in which statistical and vector calculations can be applied.

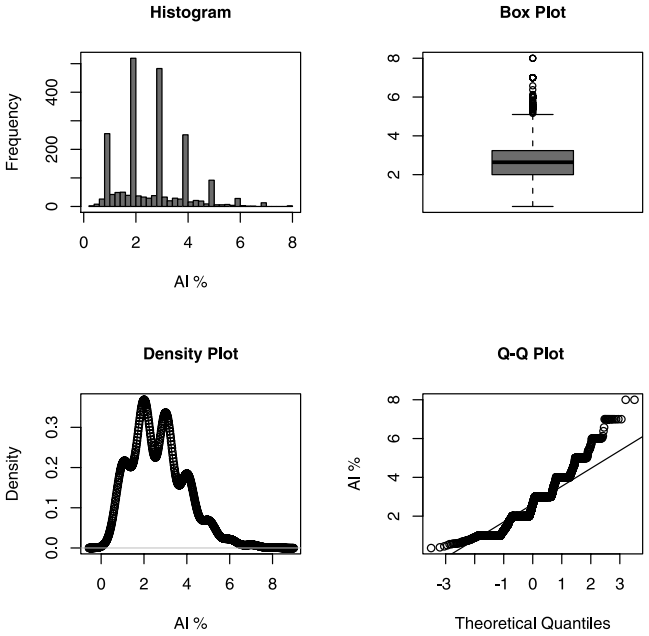


Fig. 2. Exploratory Data Analysis (EDA) plot of Al in lake sediments, Batchawana area, Ontario. Note the distinct polymodal nature of the distribution. The Q–Q plot suggests that this polymodal appearance may be due to lack of precision in the chemical analysis.

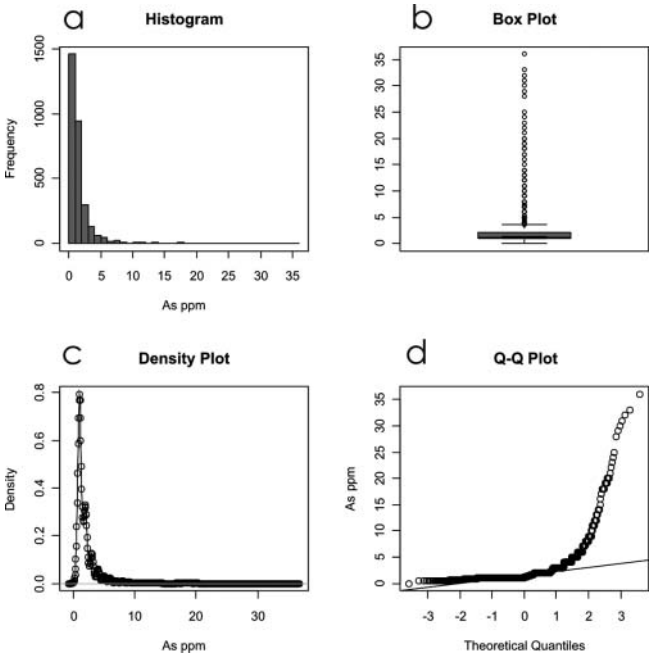


Fig. 3. Exploratory Data Analysis (EDA) plot of As in lake sediments, Batchawana area, Ontario. Arsenic exhibits a log-normal type of distribution. Extreme values (outliers) influence the shape of the distributions in all four plots.

SUMMARIZING GEOCHEMICAL DATA

Univariate data summaries

The following description of data exploration is based on examining univariate populations. EDA plots are shown in Figures 2a–d and 3a–d. These plots are often useful when grouped together as they provide different ways of summarizing data. Data summaries, in combined graphical and text form, provide a basis for context and comparison of different data types.

Histograms

The histogram is one of the most popular graphical means of displaying a distribution since it reflects the shape similar to theoretical frequency distributions. Figures 2a and 3a illustrate how the histogram can be used to display the distribution of Al and As in lake sediments. These two elements have been chosen to demonstrate two very different geochemical responses. Aluminium is ubiquitous in the lake sediments, mostly derived from aluminosilicates such as feldspars and some clay minerals (kaolinite). Aluminium abundance is largely controlled by rock types such as granites and volcanic rocks. Figure 2a illustrates the range of Al values from sediments in lake catchments. The distribution appears polymodal, which could lead to the interpretation that the lake sediments have been derived from several different lithologies. In the Batchawana area of Ontario, these lithologies are granite gneiss, migmatite, granitoid intrusions, metasediments and metavolcanic rocks. However, on closer examination, these 'peaks' appear to be artefacts of the analytical method (varying detection limits) and can create difficulties with the interpretation. Other graphical methods that are discussed below are better suited for interpreting these data.

Arsenic is much less abundant in the country rocks of the area. When it is present, it is usually associated with sulphide minerals. Relative to Al, elevated amounts of As are a 'rare event'. This is reflected in the histogram of Figure 3a where most As values are below 10 ppm. The shape of this kind of distribution is commonly thought of as 'lognormal'. However, such a distribution may be the result of mixtures of value from different distributions where the number of values in the lower range is greater than the values in the upper range.

For constructing a histogram, a number of objective procedures have been established as initial starting points for interval selection (see Venables & Ripley 2002, p. 112). If the nature of the distribution is normal or close to normal then Sturge's rule can be applied. Sturge's rule sets the number of intervals equal to $\log_2 n + 1$ where n is the number of observations. Sturge's rule does not work well if the distributions are not normal. If the number of intervals is too few, then the finer details of the distribution are smoothed over. If the number of intervals is too many, then the distribution appears discontinuous.

Histograms can be tuned by experimenting with starting points, cut-off points and interval selections. This process is subjective and when the end points and intervals are well chosen, a meaningful interpretation is likely. Conversely, if the end points and intervals are poorly chosen, an incorrect interpretation, or no significant interpretation can be obtained.

Box plots

The box plot is a method used to display order statistics in a graphical form (Tukey 1977). The main advantage of the box plot is that, unlike the histogram, its shape does not depend on a choice of interval. Providing the scale of presentation is reasonable, the box plot provides a fast visual estimate of the frequency distribution. A box plot for As in lake sediments is shown in Figure 3b.

Within a box plot, the box is made up of the median (50th percentile), left and right hinges (25th and 75th percentile, or first and third quartile). The 'whiskers' are the lines that extend beyond the box. Several variations exist on the graphical presentation of box plots. The extreme ends (maximum and

minimum values) of the data are marked by vertical bars at the end of the whiskers. Alternatively, the whiskers can extend to the 'fences', which are defined as the last value before 1.5 × midrange beyond the hinges of the data. Observations that plot beyond 3 × midrange are plotted as bars or special symbols. The location of the median line within the box gives an indication of how symmetrical the distribution is within the range of the upper to lower hinge (midrange). The lengths of the whiskers on each side of the box provide an estimate of the symmetry of the distribution. Notches can also be added to the diagram, which identify the width of the confidence bounds about the median. Notches are evident in the box plot of Figure 2b, where the distribution of Al is not highly skewed. The notches are not visible in Figure 3b because of the skewed nature of the data and the scaling of the plot.

When using these plots to compare datasets representing different lithologies, and so on, the notches provide an informal statistical analysis. If the notches do not overlap, it is evidence that the difference between the medians is significant.

Density plot

The distribution of data can also be described graphically through the use of density plots. Density plots are smooth continuous curves that are derived from computing the probability density function of the data. The density plot is similar to the histogram; however, the curve actually represents an estimate of the probability density function. Density estimation involves the use of smoothing procedures to compute the curves and is described in Venables & Ripley (2002, p. 126–132). Density curves can be modified by specifying the range of the data from which the smoothing and estimation is calculated.

Figure 2c shows a density plot for Al in lake sediments. The polymodal nature of Al is shown more clearly than in Figure 3a and b. Figure 3c shows the density plot for As where the skewed nature of the distribution is illustrated by the sharp single peak followed by a long tail.

Quantile–quantile (Q–Q) plots

Quantile–quantile (Q–Q) plots are a graphical means of comparing a frequency distribution with respect to an expected frequency distribution, which is usually the normal distribution. Q–Q plots are equivalent to normal probability plots that have been extensively used by Sinclair (1976) for the analysis of geochemical data. Stanley & Sinclair (1987, 1989) and Stanley (1987) have written extensively on the use of probability plots for dissecting populations. A general description of Q–Q plots can be found in Venables & Ripley (2002, p. 108). These plots are generated by calculating quantile values for the normal frequency distribution (value of the normal frequency distribution over the range of probability, 0.0–1.0) and then plotting these against the ordered observed data. If a frequency distribution is normally distributed, when the quantile values are plotted against the ordered values of the population, the plot will be a straight line. If the frequency distribution of the population is skewed or the population is polymodal, the Q–Q plot will be curved or discontinuous. The advantage of the Q–Q plot is that each individual observation is plotted and thus the detailed characteristics of groups of observations can be observed.

Figure 2d shows a plot for Al in lake sediments. The plot provides some insight into the nature of the data that is not shown by any of the other three plots (Fig 2a–c). The 'stepped' nature of the plot suggests that many values of the data are not continuous but are reported as discrete values rounded off at the nearest percentage value. The step-like pattern indicates that measurements were made in 1% increments for some of the data and in 0.01% increments for other data. In fact, the pattern that is observed is a mixture of four surveys, three of which have a resolution of 1% for Al, and the fourth survey has a resolution of 0.01%. The departure of the stepped plot from the straight line indicates that it is a slightly skewed distribution. Figure 2d shows the Q–Q plot for As which clearly reveals the non-normal nature of the distribution by its non-linearity. Q–Q plots are also useful for identifying extreme values at the tails of the distribution. The line that cuts through the data represents the intersection at the 25th and 75th percentiles of the data. In the case of the As data (Fig. 3d), the distribution is very skewed.

Summary statistical tables

Summary statistical tables are useful descriptions of data when quantitative measures are desired. Summary statistical tables commonly include listings of the minimum, maximum, mean, median, 1st quartile, and 3rd quartiles. Measures of dispersion include the standard deviation, median absolute deviation (MAD), and the coefficient of variation (CV). The coefficient of variation is useful because the dispersion is expressed as a percentage (the mean divided by the standard deviation), so it can be used as a relative measure to compare different elements. An example of a summary table for a selected group of elements from the lake sediment data is shown in Table 1. The table lists minimum, maximum, mean, median and selected percentile values for 35 elements and loss on ignition (LOI). Comparison of the mean and median values for each of the elements shows that many of them are significantly different from each other. This implies that the distributions for these elements are not normal and are likely skewed.

Summary tables are useful for the purpose of publishing actual values; however, graphical methods, as previously described, provide visualization about the nature of distributions and the relationships between observations. The values of a summary table are best interpreted when used in combination with graphical summaries.

Spatial presentation

It is particularly meaningful to display geochemical survey data in a geographical context. As discussed previously, GIS is a very useful tool for evaluating geochemical data during the exploratory analysis phase. Plate 6a shows a symbol plot of As from lake sediments in the Batchawana area of Ontario. Each symbol represents a collection site. The number of symbols and the symbol sizes were chosen based on an evaluation of the accompanying EDA plot in Plate 6b. An initial view of the EDA plot for As showed that the distribution was positively skewed and the plot was difficult to interpret. A $\log_{10}$ transform was then applied to the data values and the resulting EDA plot was much easier to interpret. The EDA plot of Plate 6b shows at least four distinct populations. The first population ranges in values from < -0.02–0 $\log_{10}$ scale (0.9–1 ppm) and is related to the many specimens with As values close to the detection limit. The second population ranges from 0–1.2 $\log_{10}$ scale (1–16 ppm) and reflects background As values associated with the geology. The third population ranges from 1.2–1.6 $\log_{10}$ scale (16–40 ppm) and occurs mainly in the south-central part of the Batchawana greenstone belt in an area where there is known pervasive carbonate alteration associated with shear zones. The fourth population ranges from 1.6–2.0 $\log_{10}$ scale (40–100 ppm) and represents areas where there are known sulphides.

Table 1. *Summary statistics for lake sediments, Batchawana Area, Ontario.*

Element	Units	LLD	Num Obs	Min	1%	5%	10%	25%	Median (50%)	Mean	75%	90%	95%	99%	Max	Std. Dev.	MAD	CV
LOI	weight %	2.96	3019	3	8.6	20.55	27	35	44	44	53	61	65.8	76.08	91.5	13.7	13.3	0.3
Ag	ppm	0.2	2900	0.2	0.2	0.2	0.2	0.2	0.5	0.7	1	1	1	1	72	1.5	0.4	2.3
Al	weight %	0.36	3047	0.4	0.64	0.93	1	1.52	2	2.5	3	4	5	6	8	1.2	1.4	0.5
As	ppm	0.5	3046	0.5	0.6	0.9	1	1	1.2	2.2	2	4	6	17	96	4	0.4	1.8
Au	ppb	1	3042	1	1	1	1	1	1	2.1	3	5	5	8	64	2.1	0	1
Ba	ppm	30	3047	30	50	70	80	109	148	167.8	210	290	340	440	680	85.2	71.2	0.5
Be	ppm	0.5	3047	0.5	0.5	0.5	0.5	0.5	0.5	0.8	1	1	1	2	54.1	1	0	1.3
Bi	ppm	2	3047	2	2	2	2	2	2	2.9	5	5	5	6	10	1.4	0	0.5
Br	ppm	1	3046	1	3	6	8.5	14	22	25.6	34	48	57.4	76.7	132	16.1	14.1	0.6
Ca	weight %	0.23	2685	0.2	0.43	0.56	0.66	0.89	1	1	1.04	1.35	1.58	2	9.1	0.4	0.1	0.4
Cd	ppm	0.2	3047	0.2	0.2	0.5	0.5	0.6	1	1	1	2	2	3	6	0.6	0.3	0.5
Co	ppm	1	3047	1	1	2	3	4	6	6.9	9	11	13	21	105	5	3	0.7
Cr	ppm	1	3047	1	8	12	15	20	27	31.3	38	49	63	99	328	18.2	13.3	0.6
Cu	ppm	2	3047	2	7	11	14	20	29	34.2	41	60	74	120	441	24.3	14.8	0.7
Fe	weight %	0.14	2649	0.1	0.2	0.31	0.4	0.63	1	1	1	1.7	2	4	15	0.7	0.3	0.7
Hf	ppm	1	3046	1	1	1	1	1	2	2.3	3	4	5	7	30	1.4	1.5	0.6
K	ppm	0.05	1809	0.1	0.09	0.13	0.15	0.21	0.3	0.5	0.69	1	1	1.36	2	0.3	0.3	0.7
La	weight %	1	3046	1	5	9	11	17	25	29	36	49	60	95	408	19.3	13.3	0.7
Lu	ppm	0.1	1605	0.1	0.1	0.1	0.1	0.2	0.2	0.2	0.2	0.3	0.4	1	2	0.2	0	0.7
Mg	weight %	0.04	1636	0	0.06	0.08	0.09	0.12	0.2	0.3	0.32	0.5	0.99	1	2	0.2	0.1	0.9
Mn	ppm	20	3047	20	30	42	50	70	114	159.8	195	295	415	745	3410	168	77.1	1.1
Mo	ppm	1	3047	1	1	1	1	1	2	2.3	3	4	5	10	84	3.2	1.5	1.4
Na	weight %	0.03	1999	0	0.06	0.09	0.12	0.21	0.5	0.7	1	1.25	1.94	2.19	4	0.5	0.5	0.8
Ni	ppm	3	3047	3	6	8	10	12	16	17.3	21	26	31	44	153	7.9	5.9	0.5
P	ppm	150	2197	150	260	340	400	540	820	941	1240	1630	1890	2410	4700	508.6	474.4	0.5
Pb	ppm	2	3047	2	2	4	4	6	10	11.6	14	19	22	35	1340	27.3	5.9	2.4
Sb	ppm	0.1	1627	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.1	0.2	0.3	1	7	0.3	0	1.8
Sc	ppm	0.1	3046	0.1	1.7	2.4	3	4	5	5.2	6.1	8	9	12	19	2.2	1.5	0.4
Sr	ppm	12	3047	12	21	29	32	42	60	78.3	95	153	195	276	427	54.3	34.1	0.7
Ta	ppm	0.5	3046	0.5	0.5	0.5	0.5	0.5	2	1.4	2	2	2	2	3	0.7	0	0.5
Th	ppm	0.4	3044	0.4	1	1.2	1.7	2	3	3.3	4	5.2	6	9	26	1.7	1.5	0.5
Ti	weight %	0.009	1557	0	0.02	0.029	0.032	0.047	0.1	0.1	0.103	0.137	0.16	0.21	0.3	0	0	0.5
U	ppm	0.1	3009	0.1	0.3	0.6	0.9	1	2	4.2	4.1	9.3	16	34	195.5	7.5	1.5	1.8
V	ppm	5	3047	5	7	10	12	16	24	27.1	34	46	54	79	301	15.9	13.3	0.6
W	ppm	1	3046	1	1	1	1	1	1	1.7	2	2	3	8	46	1.7	0	1.1
Zn	ppm	13	3047	13	21	36	45	62	86	98.6	118	155	184	361	952	68.1	38.5	0.7

The choice of symbol size and colour can be used to illustrate patterns of similarity and difference between several elements in the data. If the goal is to illustrate atypical observations, then once a background range of values has been established, observations that exceed the limit of the background can be assigned unique colours or different sized symbols. If the distribution of the data is non-normal and the observations of interest are in the positive tail of the distribution, then a logarithmic scale can be used to assign symbol sizes.

Kürzl (1988) and Reimann *et al.* (2005) suggest a unique approach by creating symbols based on EDA methods. Using the divisions within a box plot, the median value (Q2) and the interquartile range Q1–Q3 (r), the upper fence (Q3 + 1.5*(Q3 − Q1), the lower fence (Q1 − 1.5*(Q3 − Q1), lower outside values (Q1 − 3*(Q3 − Q1)), and upper outside values (Q3 + 3*(Q3 − Q1)) can be used to define unique symbols which express the ranking of an observation. An example of a seven-symbol set can be defined as:

1. < lower outside values
2. lower outside values to the lower fence
3. lower fence to Q1
4. Q1 to Median (Q2)
5. Median (Q2) to Q3
6. Q3 to upper fence
7. upper fence to upper outside values
8. > upper outside values 5 Q3 to Q3 + 1.5*r

Application of geostatistical techniques for evaluating the spatial continuity of geochemical processes

Contouring or imaging techniques are most reliable when the sampling density is sufficient enough so that variation between sample sites is minimal for the purposes of the sampling survey. Subjective judgment is often employed for a decision to use contouring or imaging techniques. If the sampling density is high, but the investigator believes that the geochemical response between sample sites is predictable, then contouring or imaging may be an appropriate means of visually describing the data. If the geochemical variability between sampling sites is unknown or large then it is better to use point or bubble plots as described previously. A quantitative way of assessing spatial variability can be carried out by the use of geostatistical procedures. The construction of a semi-variogram or correlogram can provide a measure of the spatial continuity/variability of a specific element. A semi-variogram measures the average variance between sample points at specific distances (lags). Generally, as the distance increases between any pair of points, the variance is expected to increase, the limit of which is the total variance of all of the data. In the correlogram, as the distance between any pair of points increases, the average correlation between the points decreases, eventually decaying to zero. Isaaks & Srivastava (1989, Chapter 4) describe a number of detailed methods for evaluating the spatial continuity of data. The effectiveness of employing geostatistical methods relies on an adequate sampling density in terms of representing the actual

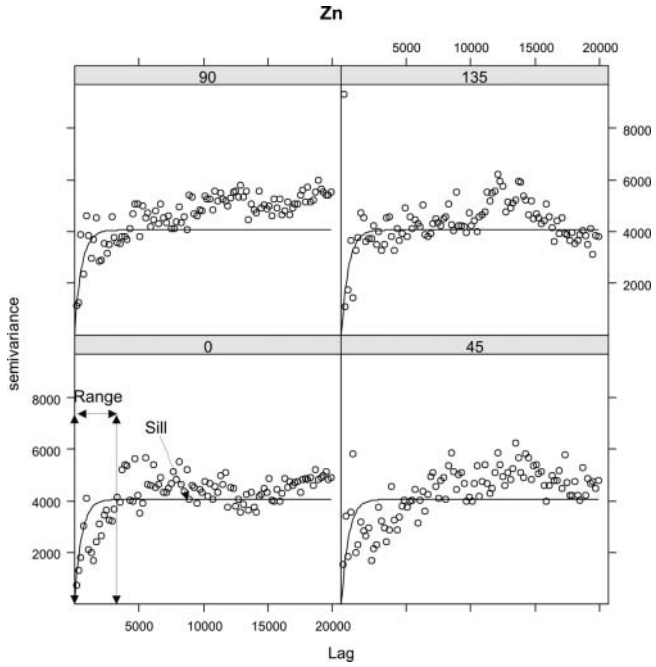


Fig. 4. Semi-variogram of Zn from lake sediments, Batchawana area, Ontario. Semi-variograms are derived for four different orientations.

variation of the data as well as the spatial distribution of the points themselves.

A large number of freeware and commercial geostatistical software packages are now available for carrying out geostatistical analysis. The website www.ai-geostats.org provides a list of software that is currently available. A geostatistical package, '*gstat*' has been written for the R programming environment (Pebesma 2004), which is freely available from the Comprehensive R Archive Network (R-DEVELOPMENT CORE TEAM) (see: www.r-project.org). Deutsch & Journel (1997) provide a library of software routines in Fortran (GSLIB). A general introductory discussion on spatial statistics can be found in Venables & Ripley (2002, Chapter 15) and Davis (2002, Chapter 5).

If the spatial sampling density appears to be continuous then it may be possible to carry out spatial prediction techniques such as spatial regression modelling and kriging. A major difficulty with the application of spatial statistics to regional geochemical data is that the data seldom exhibit stationarity. Stationarity means that the data have some type of location invariance, that is, the relationship between points is the same regardless of geographic location. Thus, interpolation techniques such as kriging must be applied cautiously, particularly if the data cover several geochemical domains in which the same element has significantly different spatial characteristics.

Evaluation of the variogram or the autocorrelation plots can provide insight about the spatial continuity of an element. If the autocorrelation decays to zero over a specified range, then this represents the spatial domain of a particular geological process associated with the element. Similarly, for the variogram, the range represents the spatial domain of an element, which reaches its limit when the variance reaches the 'sill' value, the regional variance of the element. Theoretically, at the origin (lag = 0), the variance should be zero. However, typically, an element may have a significant degree of variability even at short distances from neighbouring points. This variance is termed the 'nugget' effect.

Figure 4 displays four semi-variograms for Zn from the Batchawana lake geochemistry survey data covering an area of 95 km (east–west) and 62 km (north–south). Semi-variograms have been calculated for four preferred orientations: east–west, (0°), north–south (90°), NE–SW, (45°) and SE–NW (135°), using a search angle tolerance of 22.5°. The *y*-axis of each figure is the semi-variance and the *x*-axis is the lag interval. The maximum lag distance was chosen as 20 000 m and the lag interval was selected as 200 m. The selection of a suitable lag distance can be made by visually examining the distribution of sample sites; geostatistical software packages can also determine optimum lag intervals. These figures were generated using the *gstat* package from R. Each figure has been fitted with an exponential model. The most regular semi-variograms appear for the 135° and 90° orientations. This is no surprise given that that there are two primary stratigraphic orientations in the area, one trending east–west and the other trending SE–NW. The orientations of 0° and 90° display different nugget values, with the lowest nugget occurring with the east–west orientation, also suggesting better correlation between adjacent points in that direction. All four semi-variograms display periodicity, which indicates that there is heterogeneity in the spatial structure of the data, most likely reflecting changes in the underlying geology (granite vs. greenstone).

The use of kriging makes some assumptions about the spatial uniformity (stationarity) properties of the data. In many cases, particularly in regional sampling programmes, there are several lithological domains in which elements have different spatial ranges. Kriging can account for various types of spatial drift in datasets; however, the error in the kriged estimates tends to increase.

The use and application of geostatistical methods is a combination of art and science. Skill, knowledge and experience are required to use geostatistical techniques effectively. It requires considerable effort and time to model and extract information from spatial data. The benefit of these efforts is a better understanding of the spatial properties of the data which permits better estimates of geochemical trends. However, they must be used and interpreted with the awareness of problems with techniques of interpolation and the spatial behaviour of the data.

Fractal methods

The use of fractal mathematics is playing an increasingly important role in the geosciences. Carr (1994) gave a good introduction into the use of fractal methods in the geosciences. Cheng & Agterberg (1994) have shown how fractal methods can be used to determine thresholds of geochemical distributions on the basis of the spatial relationship of abundance. They have shown that where the concentration of a particular component per unit area satisfies a fractal or multifractal model, then the area of the component follows a power law relationship with the concentration. This can be expressed mathematically as:

$$A(\rho \leq v) \propto \rho^{-\alpha 1}$$

$$A(\rho > v) \propto \rho^{-\alpha 2}$$

where $A(\rho)$ denotes an area with concentration values greater than a contour (abundance) value greater than ρ. This also implies that $A(\rho)$ is a decreasing function of ρ. If ν is considered the threshold value then the empirical model shown above can provide a reasonable fit for some of the elements.

In areas where the distribution of an element represents a continuous single process (i.e. background) then the value of α remains constant. In areas where more than one process has resulted in a number of superimposed spatial distributions,

there may be one or more values of α defining the different processes.

An example of the use of concentration v. area plots is shown for As derived from lake sediments collected over the Batchawana area. Plate 7 shows a colour contoured image of As values superimposed on the sample sites, and, as well, a plot of $\log_{10}$ As concentration v. $\log_{10}$ area occupied by each contour interval. Distinct changes in the slope of the plot represent breaks based on the spatial distribution of the data and each break represents a threshold between populations of data possibly derived from different processes. There are three distinct trends shown on the concentration–area plot of Plate 7. The regional background is characterized by a straight line of points ranging from 0.7 (5 ppm) to 1.3 (20 ppm). Interpolated As values greater than 5 ppm and less than 20 ppm are shown as red, blue and cyan. This represents the regional background of the area. The group of points that form a straight line from 1.3 (20 ppm) to 1.6 (40 ppm) represent the next population reflecting As associated with mineralization and anthropogenic effects. Anthropogenic effects are prevalent in the eastern part of the map area, whereas As values associated with potential mineralization are shown in the central and western part of the map area. Values above 1.6 (40 ppm) represent a small population of observations that are greater than 40 ppm (shown as orange and red on the map). These observations occur in the SE portion of the map area and may represent areas of mineralization.

Cheng *et al.* (2000) have also implemented the use of power-spectrum methods to evaluate concentration–area plots derived from geochemical data. By the application of filters, patterns can be detected related to background and noise, thus enabling the identification of areas that are potentially related to mineralization. More details on this methodology can be found in Cheng (2006).

Multivariate data summaries

Scatterplot matrix

The ScatterPLOt Matrix (SPLOM) is a useful graphical multivariate method for visually assessing the relationships between variables. When categorical information is available, colour can be used to show differences between the categories.

Two areas were chosen from the Ben Nevis mapsheet (Plate 8): one representing an area of carbonate alteration and the other, an area of metavolcanics without carbonate alteration. Figure 5 shows a scatterplot matrix of a selected number of elements from the two areas. The matrix highlights associations and patterns in the data. There is a clear distinction between the altered and unaltered observations for CO_2 with Co, Cu and Cr. CO_2 shows an overall increase for the altered specimens, whereas the abundances of Cu, Cr and Co vary widely in a suite of specimens from the carbonate alteration zone. The distribution patterns for these elements can be studied further using other graphical measures such as box plots.

Multiple box plots

In Figure 6, box plots for nine elements from the Ben Nevis lithogeochemistry data show that there are clear differences in the geochemistry between the two areas. Box plots are a convenient way of summarizing the differences between groups of data. Note that there is a distinct shift in the median value data for CO_2 and Li (an increase) and a corresponding decrease in Ca and Sr for the specimens from the altered area. This is consistent with studies that indicate that there is overall loss of Ca and Sr in the zone of carbonate alteration, and an increase

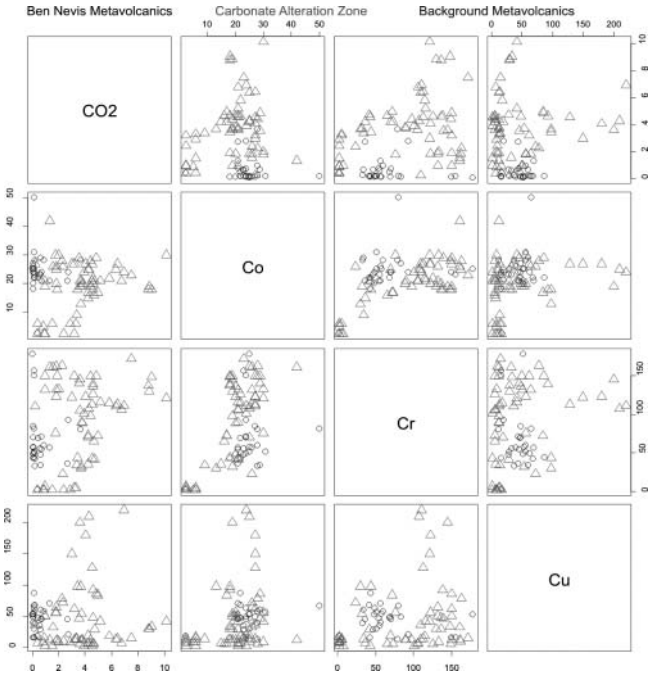


Fig. 5. Scatterplot matrix of altered and unaltered metavolcnics from the Ben Nevis area of Ontario. Carbonate altered rocks cluster differently from the non-altered rocks.

of Li and Na. Chromium, Na, Ni, Cu and Co show greater variability in the altered area. The greater variability is due to a breakdown of the original mineralogy accompanied with the addition of CO_2, Si, Li, Cu and several other elements that are associated with hydrothermal activity and mineralization.

Lattice graphics

Lattice graphics is a special graphics library in R that enables multivariate summaries of data for more effective visualization and subsequent interpretation (Sarkar 2008). For example, a correlation matrix can be expressed graphically as illustrated in Plate 9: this is a graphical expression of the correlation matrix of the lithogeochemical data from the Ben Nevis, Ontario area.

The colour ramp, on the right side of the figure, gives the scale of the correlation coefficient −1 (blue) to +1 (red). Thus the positive, negative and neutral associations of the elements can be quickly assessed.

DIFFERENTIATING GEOCHEMICAL BACKGROUND FROM ANOMALIES

The recognition of a geochemical anomaly requires that a geochemical background has been established, which in itself can be difficult to define. Geochemical values that depart from the background, that is, those values which are atypical, may be anomalous. Howarth & Sinding-Larsen (1983, p. 208) discuss the concept of anomaly and suggest that anomalous concentrations are those values that exceed a given threshold. Workshops held by the Association of Exploration Geochemists (AEG) in 1983 and 1985 (Garrett 1984; Aucott 1987) failed to give any formal definitions and concluded that an anomaly is a desired level of abundance in which the geologist has a particular interest and is different from the regional or background values. Joyce (1984, p. 15) discusses the definition of an anomaly in terms of an adequate definition of background.

Historically, values exceeding the 98th percentile were scrutinized for their potential to be identified as geochemical

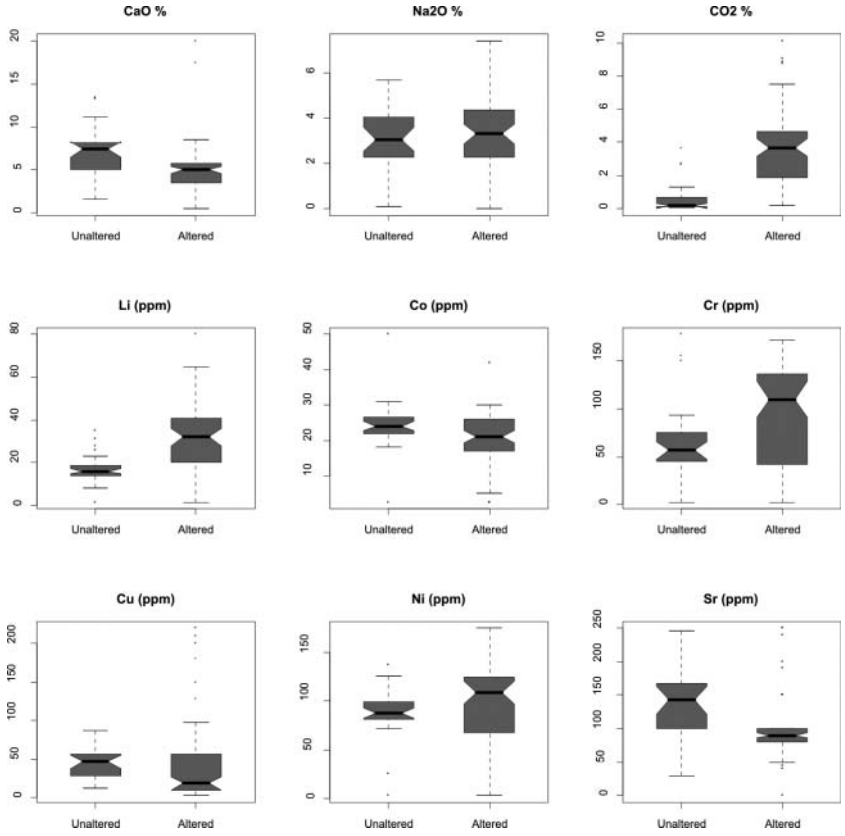


Fig. 6. Box plots showing the character of selected elements between the altered and unaltered sites.

anomalies. As well, the threshold was defined as the mean ± 2 standard deviations (Hawkes & Webb 1962; Howarth 1983, p. 208). This definition was based on the assumption of normality of the data. However, with the introduction of computer-based methods for evaluating geochemical data, the ability to study sample populations and the nature of geochemical distributions has provided powerful tools for the identification of outliers and specimens that might be related to mineralization targets (anomalies). As a result, the use of choosing thresholds based on the calculation of the mean ± 2 standard deviations is no longer recommended (see Rose *et al.* 1979; Levinson 1980; Garrett 1989*b*). Filzmoser *et al.* (2005) describe an approach to outlier and anomaly detection using robust methods and adaptive techniques for recognizing outliers.

The threshold and pathfinder elements

An important goal of the investigation of geochemical data is the detection of spatially continuous zones of elevated values of a strategic element that exceed a specified threshold value. Observations that exceed the threshold are termed 'anomalies'. Joyce (1984, p. 9–13) provides a detailed description of indicator and pathfinder elements and minerals that can be used in exploration strategies. Garrett (1991) defined the threshold as the outer limit of background variation; the term 'outer' is used instead of 'upper'. This allows the definition to include both 'upper' and 'lower' limits, as it is common in some geochemical environments for depletion haloes to be as important as enrichment haloes. Reimann *et al.* (2005) further refined the definition of threshold and background based on robust methods.

The concept of threshold can be extended from single element to multi-element data by the use of multivariate statistical methods such as the use of the Mahalanobis distance (Garrett 1989*c*). In the multivariate case, the threshold can be selected on the basis of examination of Mahalanobis distance plots or some other more robust measure of background and departures from it.

Observations from distributions that represent processes of interest (mineralization or anthropogenic effects) usually overlap with observations from background distributions such that the threshold is more likely a range of values where the two distributions overlap. Rather than choose a specific threshold value, it may be better to assign a probability of the likelihood of an unknown specimen belonging to each population. In geochemical surveys, anomalies have a spatial association and are small and only occupy a fraction of the area that is covered by the regional population.

Plate 10 shows the threshold as determined by a visual inspection of the Q–Q plot. In this case, the threshold for K_2O is chosen at 2.5 %, which is considered above the usual range of values for volcanic rocks. The values that exceed the threshold can be identified on the map by choosing a symbol size or colour to identify them.

Mineral deposits are often characterized by a unique suite of elements whose values exceed the threshold of the surrounding background material. These elements are called pathfinder elements and often have a greater spatial extent relative to the target being sought. In the Ben Nevis metavolcanic sequence, K can be considered as a pathfinder element. Elevated values of K are typically associated with epithermal Au deposits. Examination of the distribution of K_2O in Plate 10b suggests that values above 2.5 wt% K_2O are atypical and that value defines the threshold. The map of K_2O values in Plate 10a indicates that K_2O values greater than 2.5 wt% are associated with the two known mineral occurrences as well as several other sulphide-bearing occurrences.

Outliers or anomalies?

An outlier can be defined as an observation with a value that is distinctively different from observations with which it is

intimately associated. If a threshold has been defined, then an outlier, by default, exceeds the threshold. Outliers may be of significance from an exploration or contamination point of view. An outlier may define a mineralized zone (anomaly) or a value that is above an accepted environmental background level. Outliers can also be artefacts of erroneous analytical results or data entries. An outlier can be identified as a geochemical anomaly if it exceeds the threshold, is not the result of an analytical problem, or assigned to an improper population. In other words, an anomaly is associated with a process of interest (alteration or mineralization), whereas an outlier is a value without an interpretation that requires further assessment.

Outliers should always be examined carefully to be certain that the observed values are not the result of an error. An observation that is an outlier in one group may be indistinguishable (masked) from other observations within another group. In practice, outliers are assessed by a graphical examination of the upper and lower rankings of the data and the identification of observations that occur as distinct breaks from the background population. The application of a transformation may be sufficient to separate the background from outliers.

Plate 11a shows a Q–Q plot of As from the lake sediment data. Arsenic, a pathfinder element, is commonly associated with gold deposits. An examination of the plot shows that 'breaks' occur at the approximate values of 20, 25 and 35 ppm. In comparison with the fractal approach, the break at 20 ppm is equivalent to the abrupt change in slope in Plate 7, where the concentration–area plot identifies a distinct change in the data population at a value of $\log_{10}$As=1.3 (19.95 ppm). These breaks most likely represent distinct populations that can be attributed to different source lithologies. The breaks are used as the basis for a change in symbol sizes on the map of Plate 11b. There are six extreme values that occur above the level of 35 ppm, which is considered to be the threshold. These values can be considered as anomalies because of the break in the slope of the curve and the distance between these values and the bulk of the population. These outliers would be of interest in a mineral exploration programme.

In the case of two or more (multi-modal) populations it is necessary to decompose the populations into separate distinct populations through the analysis of Q–Q plots, probability plots or by computer-based means (Sinclair 1976; Stanley 1987; Bridges & McCammon 1980). Garrett (1989*c*), Filzmoser *et al.* (2005) and Filzmoser & Hron (2008) have developed methods for outlier detection in multivariate data using a multivariate outlier plot, which identify observations that appear to belong to a population different from the main population. This has obvious benefits in evaluating geochemical data for observations associated with alteration or mineralization.

Truncated and censored data

When an analytical procedure detects the presence of an element, but the value is too low to be accurately quantified, the value is reported as 'less than the limit of detection' (lld). The same applies for values that exceed the upper limit of detection. The lower/upper limits of detection are the limits of reliable quantification by the analytical procedure. Typically, a laboratory will report the value prefixed with a '<' for a value less than the lld or '>' for a value that exceeds the upper limit of detection. When a group of values contains observations that exceed the detection limits, the effect is called 'censoring'.

Figure 7 shows the distribution of Co in metavolcanics collected during a lithogeochemical sampling programme in the Ben Nevis township area of Ontario. The analytical procedure

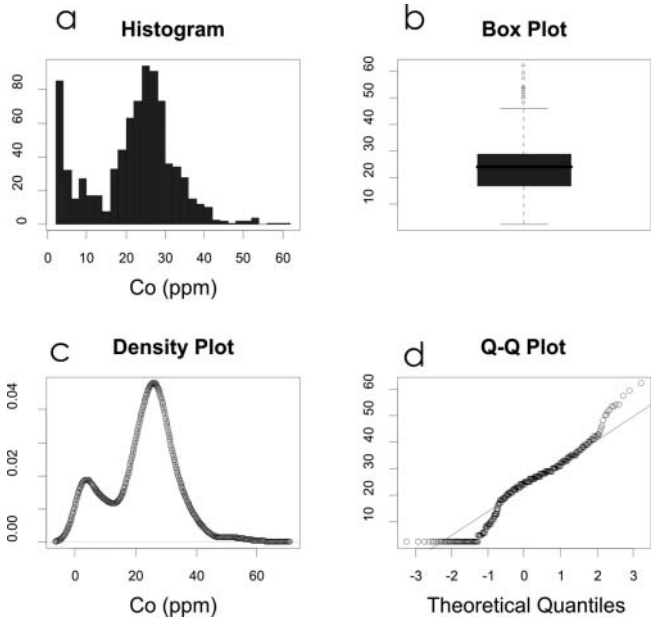


Fig. 7. Cobalt (ppm) in metavolcanics, Ben Nevis Township, Ontario, Canada.

for Co has a lower limit of detection of 5.0 ppm and 85 out of the 824 observations fall below that limit. The histogram of Figure 7a shows a bar with a high frequency of observations at the lowest end of the scale. This bar represents the 85 values that are less than the detection limit. The Q–Q plot (Fig.7d) shows these values as a flat part of the distribution at the left side of the figure. The box and density plots (Fig. 7b, c) do not show the censored values as clearly. Historically, censored data were handled by applying a substitute value, somewhere between 1/3 to 1/2 of the actual detection limit. As the number of observations below the lld (censored) increases, then this estimate will produce inaccurate estimates of the mean and variance (see Sanford *et al.* 1993).

Several techniques have been developed to minimize the problem of censored data. The problem of censored data becomes more important when means of elements and covariances between elements are required. Using an arbitrary 'replacement' value (i.e. 1/2 or 1/3 the lld) can introduce bias in the computation of the moments of the distribution. However, if the nature of the distribution can be assumed as normal, then the replacement value of the censored data and parameters of the distribution (mean, variance) can be estimated based on the portion of the distribution that is not censored. The process of finding suitable replacement values is known as 'imputation' in the statistical literature. Estimates of the distribution parameters are obtained using the EM algorithm (Dempster *et al.* 1977), and is discussed by Chung (1985, 1988, 1989) and Campbell (1986). From these characteristics, an estimate can be made as to how the data are distributed below the lld. The assumption of normality is essential for the EM algorithm to work. Campbell (1986) invokes an algorithm to transform the data to normality using Box-Cox. Sanford *et al.* (1993) have developed a method that allows for the calculation of a suitable replacement value based on a maximum likelihood approach. Helsel (1990) provides a detailed discussion on dealing with missing data in environmental studies. Chung (1985, 1989), Campbell (1986) and Lee & Helsel (2005, 2007) have published computer procedures that estimate the mean and variance of censored distributions by calculating a replacement value that is derived from the characteristics of the uncensored portion of the sample population. Dickson & Giblin (2007) have used self-organizing maps as a means of finding suitable replacement values.

Robust estimation

The presence of extreme or atypical values in a sample population can have a dramatic effect on the estimation of the mean and variance, which in turn will affect the estimation of correlation and covariance with other variables. As these measures of association are used by many statistical techniques, it is useful to minimize the influence of atypical observations. Methods of robust estimation are primarily concerned with minimizing the influence of observations that are atypical. There are several methods for determining robust estimates of location (mean/median) and scale (variance). Robust estimation procedures can be applied to both single and multivariate populations. Good reviews on robust statistics can be found in Venables & Ripley (2002, Chapter 5.5) and Daszykowski *et al.* 2007).

Geochemical distributions are often positively skewed and lognormal in appearance. The skewed nature is commonly attributed to a mixture of different populations and/or the presence of outliers. For such distributions, a robust estimate of the mean will be less than the standard estimate of the mean because the influence of the long tail and outliers is reduced.

Methods for robust estimation of location and scale include trimmed means, adaptive trimmed means, dominant cluster mode, L-estimates, M-estimates and Huber W-estimates (see Grunsky 2006).

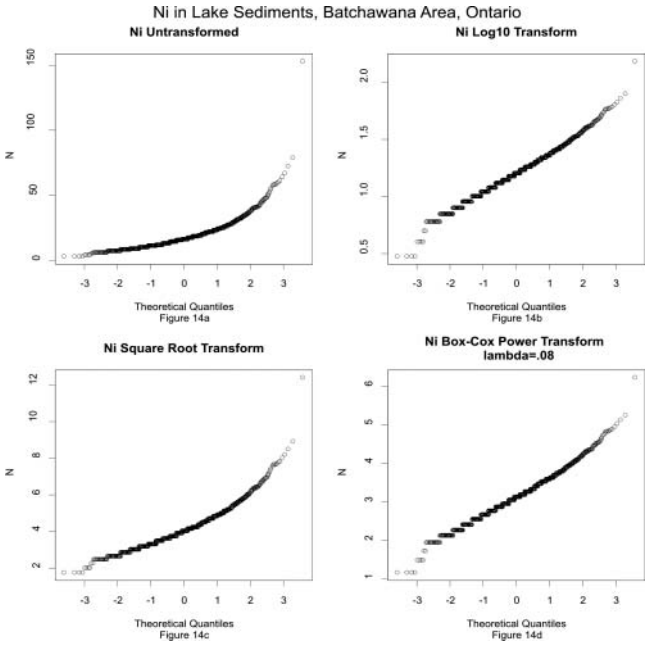


Fig. 8. Ni in lake sediments, Batchawana area, Ontario.

Transformation of data

Statistical testing and comparison between groups of data usually requires the estimation of means, variances and covariances. Most statistical procedures assume that the populations being tested are normal in nature. If there are outliers (extreme data values) or a mixture of populations (polymodal or skewed distributions) then the assumption of normality is violated. In right-skewed distributions (the most common effect observed with geochemical data), estimates of the mean exceed the median value. Similarly, the estimation of the variance is inflated for a skewed distribution. The skewed nature of the data can be overcome by applying a suitable transformation that shifts the values of the distribution such that it becomes normally distributed. It has been common in the geological literature to apply logarithmic transformations to data as a way to correct for a positive skew. The application of transformations to data should be carefully applied to avoid masking the presence of multiple populations and outliers (Link & Koch 1975). If transformations are applied to data to minimize the effect of skewness, then Q–Q plots of the transformed data should be examined for changes in slope or breaks in the line, as these features might suggest the presence of two or more populations.

Transformations that can be applied are:

- linear scaling

$$y = kx \text{ or } y = (x_i - \bar{x})/s$$

where s is the standard deviation,

- exponential $y=e^x$
- Box-Cox generalized power transform

$$y = (x^\lambda - 1)/\lambda,\ y = \ln(x) \text{ for } \lambda = 0.$$

The linear scaling transformations do not change the shape of the distribution; however, the degree of dispersion (variance) can change. The logarithmic, exponential, and Box-Cox generalized power transforms, or $\log_{10}$ modify both the shape and the dispersion characteristics of the distributions and are the transformations most commonly used. Howarth & Earle (1979) provided a computer program for estimating parameters for the generalized Box-Cox power transform based on the optimization of skew and kurtosis and the optimization of the maximum likelihood criterion of Box & Cox (1964). Lindqvist (1976) published a computer program (SELLO) for transforming skewed distributions based on minimizing skew.

In EDA, transformations are useful in assessing whether outliers are the result of a non-normal frequency distribution or are truly atypical values. The distribution should be examined for outliers both before and after a transformation has been applied to the data. Once any outliers are eliminated, the data should be re-examined for outliers as above until all are identified and eliminated. Campbell (1986) prepared computer programs that account for atypical values in the estimation of transformations and robust estimates of means and variances. Stanley (2006) discusses the application of transformations to maximize geochemical contrast and improve data presentation.

Figure 8 shows the effect of applying four different transformations on Ni for lake sediments from the Batchawana area of Ontario. The data are represented on Q–Q plots. Figure 8a shows the untransformed data; Figure 8b shows the $\log_{10}$ transformation of the data; Figure 8c shows a square root transformation; and Figure 8d shows a Box-Cox generalized transformation with a value of λ determined after the top 5% of the data were trimmed. The resulting value of λ=0.08 is close enough to zero that there is little difference between the log transform of Figure 8b and 8d.

Discussions on the application of transformations of geochemical data have traditionally been based on raw analytical values and the potential problems associated with closure have not been taken into account. Further research is required in this field.

LEVELLING GEOCHEMICAL SURVEY DATASETS

Regional exploration programmes and integration projects often involve the assembly of diverse sets of data. A common problem associated with the assembly of geochemical survey datasets is known as levelling. Levelling involves the adjustment of values of an element from one survey to be similar to the

values of another survey. This 'similarity' implies that the means, medians and variations are similar, or in other words, have the same parametric characteristics. Levelling geochemical survey data involves many assumptions and is mitigated by many factors, which are discussed below.

In many geochemical studies, the integration of several sets of data is necessary. Geochemical surveys may have been carried out over an extended period of time during which field sampling methods, sample preparation, methods of digestion and analytical instrumentation may have changed. Thus, there is the potential for a large degree of heterogeneity in the data that is not based on the underlying geology. It is not advisable to level the results of geochemical data derived from different methods of collection (media), preparation (digestion) or analytical methods. The detection limits may be different and there may be systematic shifts between the groups of data. In order to use these data effectively, one or more sets of data must be adjusted. This is known as levelling. One set of data is chosen against which all other sets of data will levelled. The relationship of each element is compared and an adjustment is made through the application of a linear transformation. Given an observation x, with (i=1, . . .n) variables,

$$y_i = ax_i + b$$

x_i is the unadjusted variable for observation x,
y_i is the adjusted variable for observation x,
a represents the slope of the line in the transformation,
b represents the intercept or additive adjustment.

The adjustment can be determined through regression methods. Non-linear transformations may also be applied if necessary. Figure 9 shows the types of levelling scenarios that can be encountered. The x and y axis of each figure shows the values of the quantiles (values at 5, 10, 15, etc. percentiles) for the two variables. With exception of Figure 9e, each scenario shows a possible relationship that will permit levelling. Figure 9e shows a random association between the two variables and in this case levelling is not possible. A detailed example of levelling geochemical data is provided below.

There are several challenges in levelling data, the first of which is the choice of data against which to level everything else. Considerable time should be spent on assessing the variability of each element across all of the surveys to be levelled. There may or may not be one set of survey data that can be used as the benchmark dataset, for all elements. Choosing when an element requires levelling must be carried out with caution. Comparing values on maps using bubble plots can be misleading, unless the data are evaluated using the same range and scaling.

Assembling a large number of geochemical surveys and evaluating the need for levelling can be a challenging problem. Trepanier (pers. comm. 2006; Identifcation de domains géochemiques à partier des levés régionaux de sediments de fond de lacs, Projet 2004–09. Presentation at the Consortium de recherche en exploration minérale) developed an iterative and adaptive method for levelling a large number of surveys. The method assumes that, for each element, one set of survey data represents the standard by which all other surveys will be levelled. All data are stored in a database and an automatic procedure is invoked to search through and adjust the data for each element. The method is computationally intensive and time-consuming.

As shown in Figure 9, there are four typical scenarios for levelling between two datasets. Note that in Figure 9, the values that are plotted are the values at specified quantiles of the data (i.e. 5, 10, 15, . . . 90, 95th percentiles). The worst possible scenario is shown in Figure 9e where no levelling is possible because no linear relationship exists between the two sets of data. It is also possible that a non-linear shift or multiplier will level two datasets. Graphical inspection of quantile plots between two sets of data should be carried out prior to assessing the type of levelling required.

Daneshfar & Cameron (1998) have demonstrated a method of levelling geochemical data described in Darnley *et al.* (1995) that accounts for the geology that underlies geochemical data survey sites. The method requires the use of GIS and a statistical package that computes quantiles and linear regression.

A strategy for levelling several datasets involves the determination of which dataset should be chosen for all of the other databases to be levelled against. The choice of this dataset, the 'standard dataset', will depend on the following factors: spatial proximity of the two datasets; accuracy and precision of the standard dataset; and that the standard dataset contains enough specimens and enough elements so that the other datasets can be levelled to it.

The integration of geochemical survey datasets requires the identification of several key parameters so that the data can be accurately interpreted, that is: type of media; method of preparation; method of digestion; method of analysis; and lower and upper limits of detection.

If levelling involves geochemical datasets where these characteristics are different then it may be unwise to attempt to level the data. An alternative approach is to map the departure from the median or some other measure that characterizes individual specimens against the distribution for a particular area. Non-spatial levelling is often required (i.e. adjusting location and scale) to remove boundary effects and the comparison of different analytical methods. The following discussion describes some of the challenges associated with levelling geochemical survey datasets.

The lower and upper limits of detection are commonly different between geochemical survey reports. This is due to

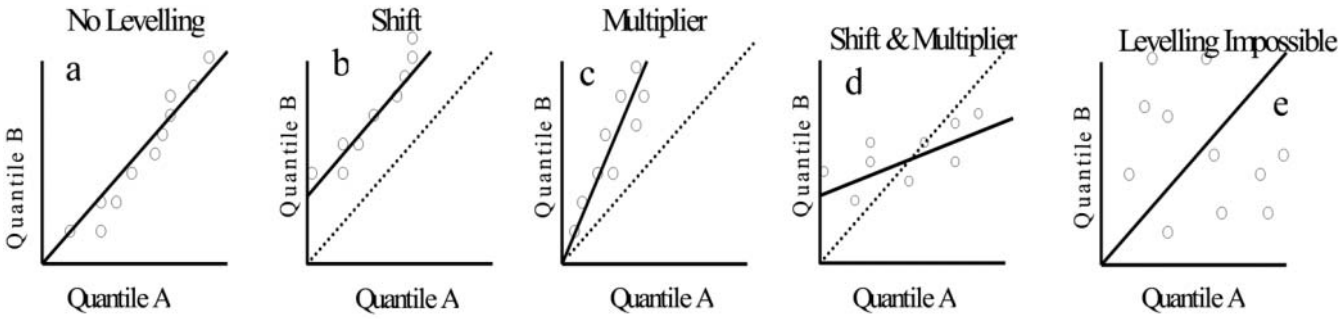


Fig. 9. Levelling scenarios for geochemical data.

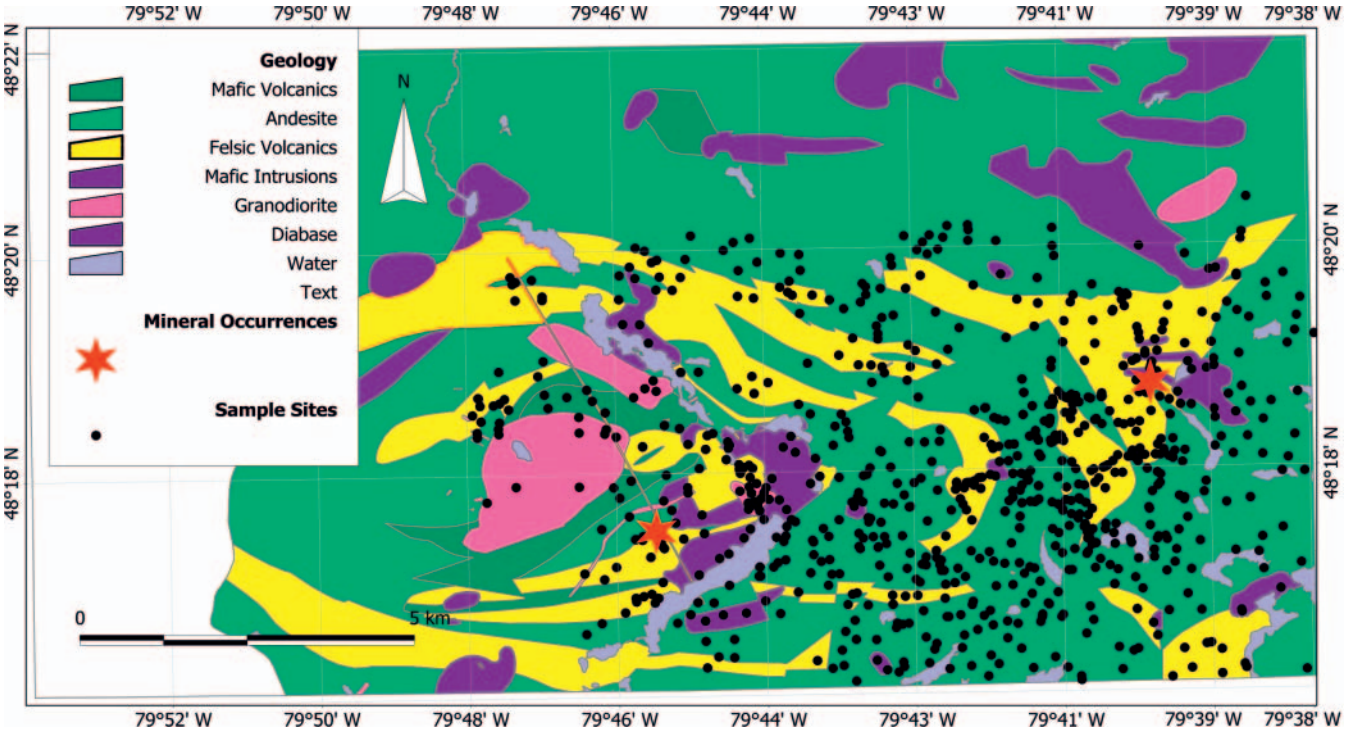


Plate 1. General geology of the Ben Nevis Township area, Ontario, Canada.

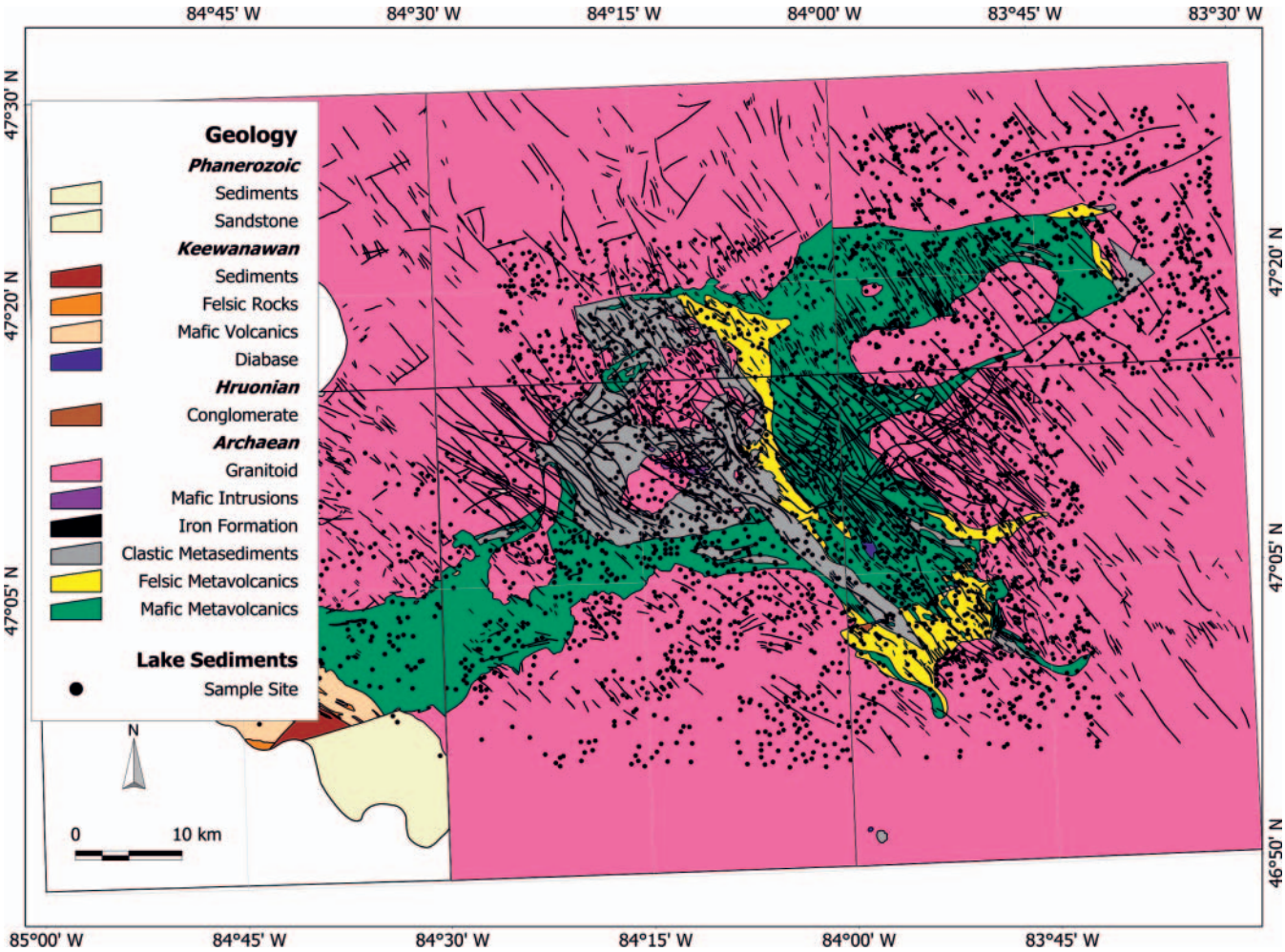


Plate 2. General geology of the Batchawana area, Ontario, Canada.

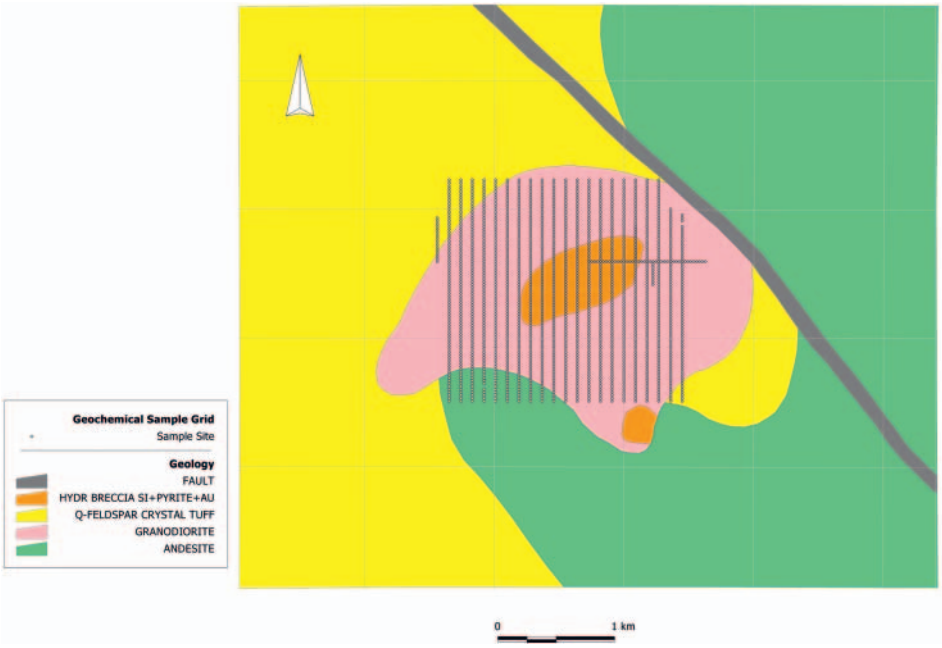


Plate 3. Location of the soil survey area, Island of Sumatra, Indonesia.

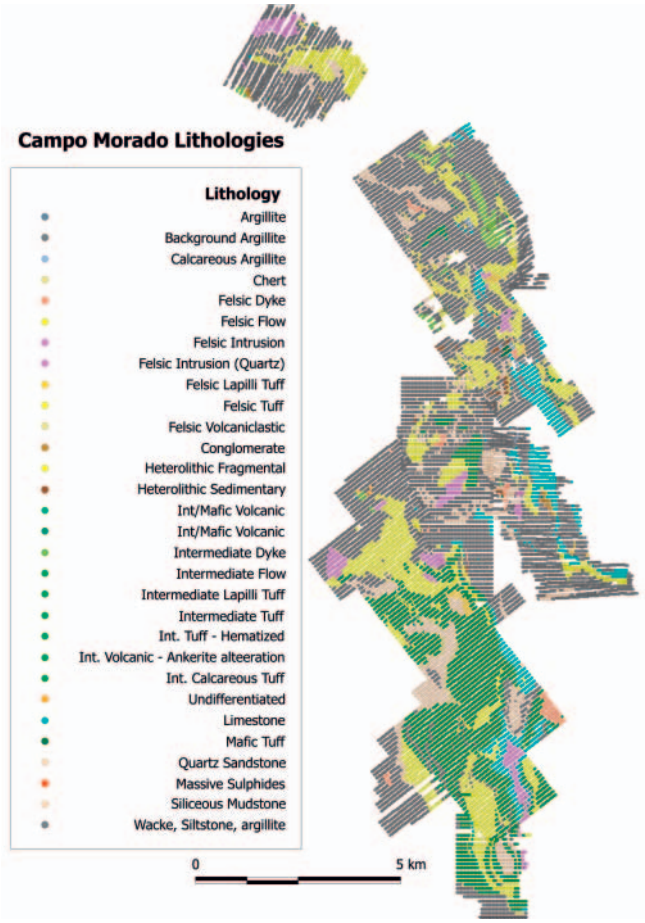


Plate 4. Lithologies of the Campo Morado area, Mexico.

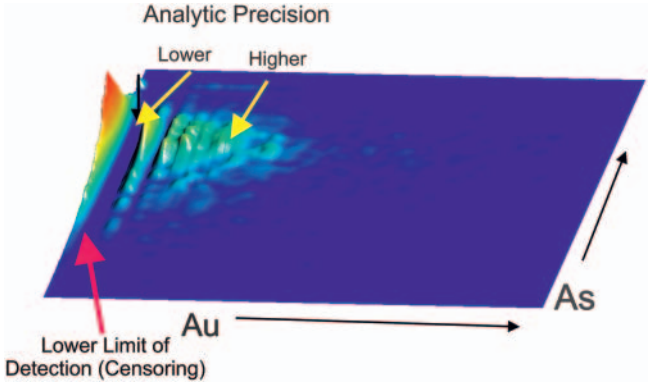
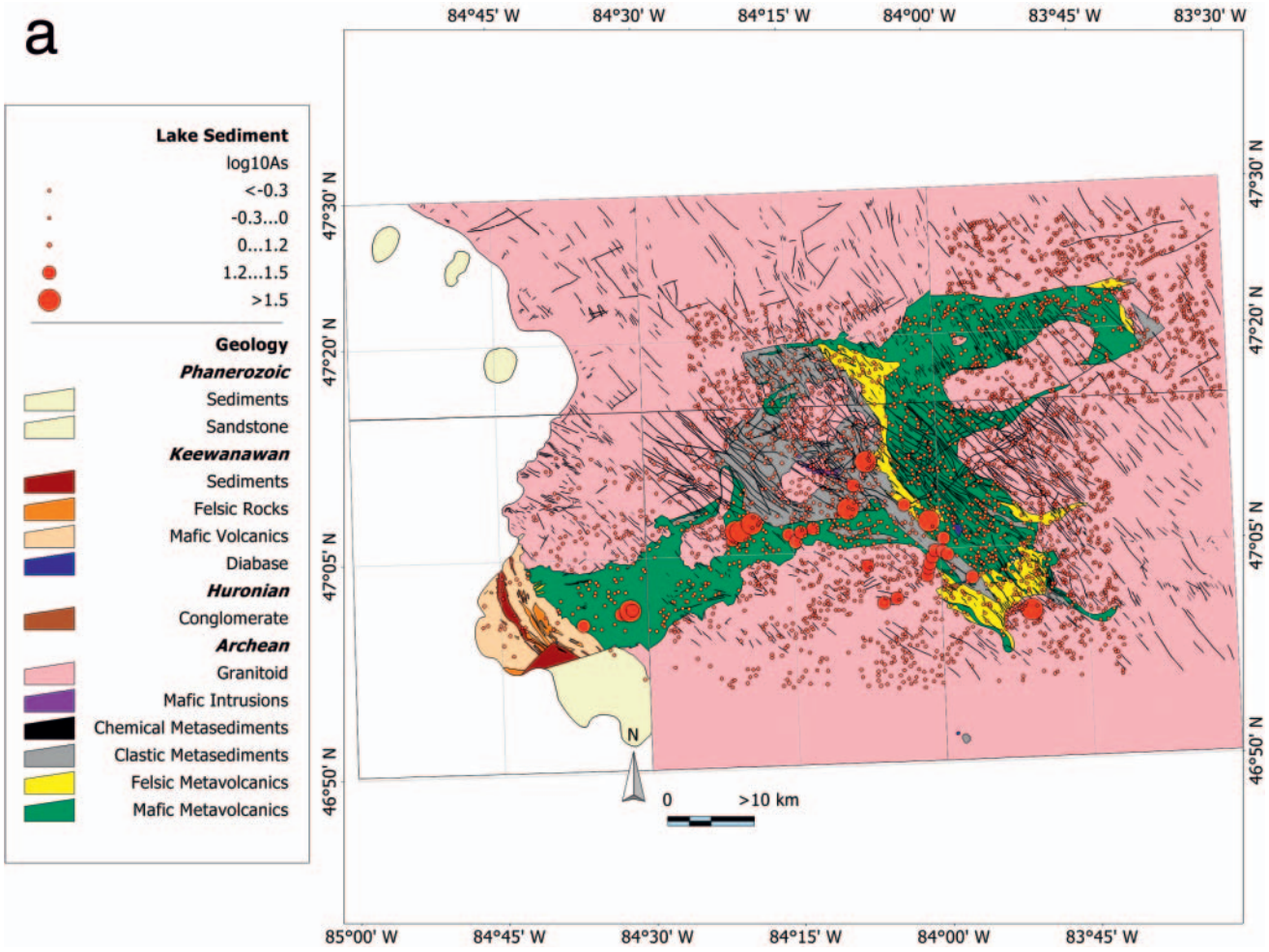


Plate 5. Density plot of arsenic versus gold displaying censoring and quantization of the analytical data.

the nature of the method of analysis and the developments in the analytical procedures that have taken place over time. As the technology of geochemical analysis improves, the lower limits of detection also decrease. Thus, when merging geochemical survey datasets, the choice of a replacement value for the lower limit of detection (lld) may become an issue. A straight replacement method of a single value will not be sufficient because the replacement value is used only to ensure a better estimate of the mean and variance of the data. Varying detection limits within a large dataset assembled from many sources may create significant problems when deciding on a replacement value. One approach is to set the lower limit of detection at the weighted median value for the range of llds in the dataset. A replacement value can then be determined based on the number of observations and associated llds.

Levelling geochemical survey datasets: an example using lake sediments in Northern Ontario

Plate 12 shows sites for five different lake sediment surveys in the Batchawana greenstone belt of Northern Ontario. These five surveys were collected during the 1980s by Fortescue & Vida (1989, 1990, 1991*a*, *b*). Hamilton (1995) describes the results of the survey conducted by Fortescue in the Cow River Area. The area is an Archaean volcano-sedimentary terrane within the Abitibi-Wawa subprovince of the Superior Province. The geology of the area is described by Grunsky (1991).



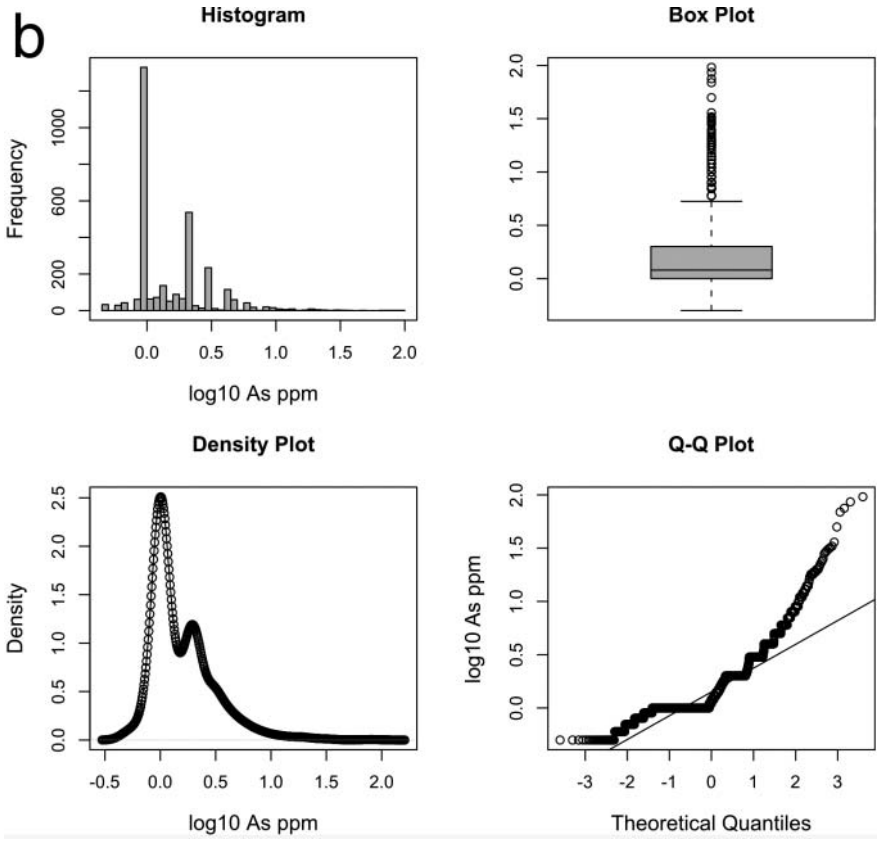


Plate 6. (**a**) Exploratory data analysis of arsenic in lake sediments, Bathawana area, Ontario. (**b**)Arsenic (log_{10}) in lakes sediments, Batchawana area, Ontario.

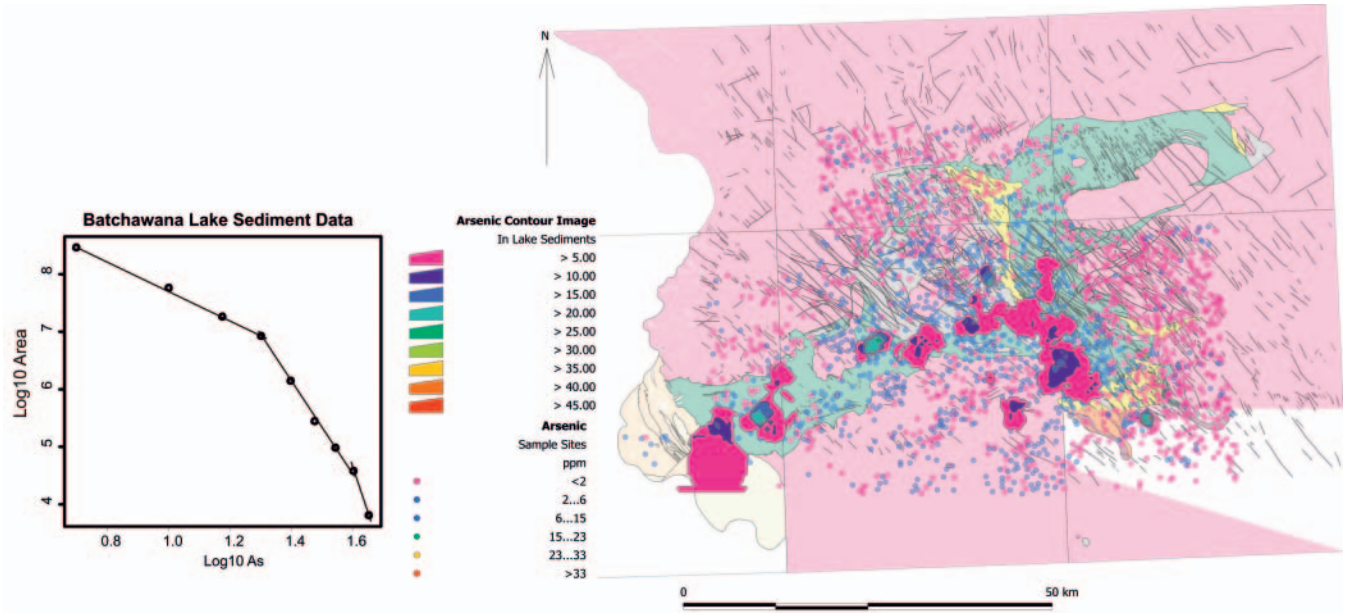


Plate 7. Arsenic from lake sediments, Batchawana area, Ontario. The contoured image reflects the area associated with each As contour level. The corresponding concentration–area plot display changes in slopes, which reflect changes in spatial patterns. These changes are associated in differences in geology, anthropogenic effects and mineralization.

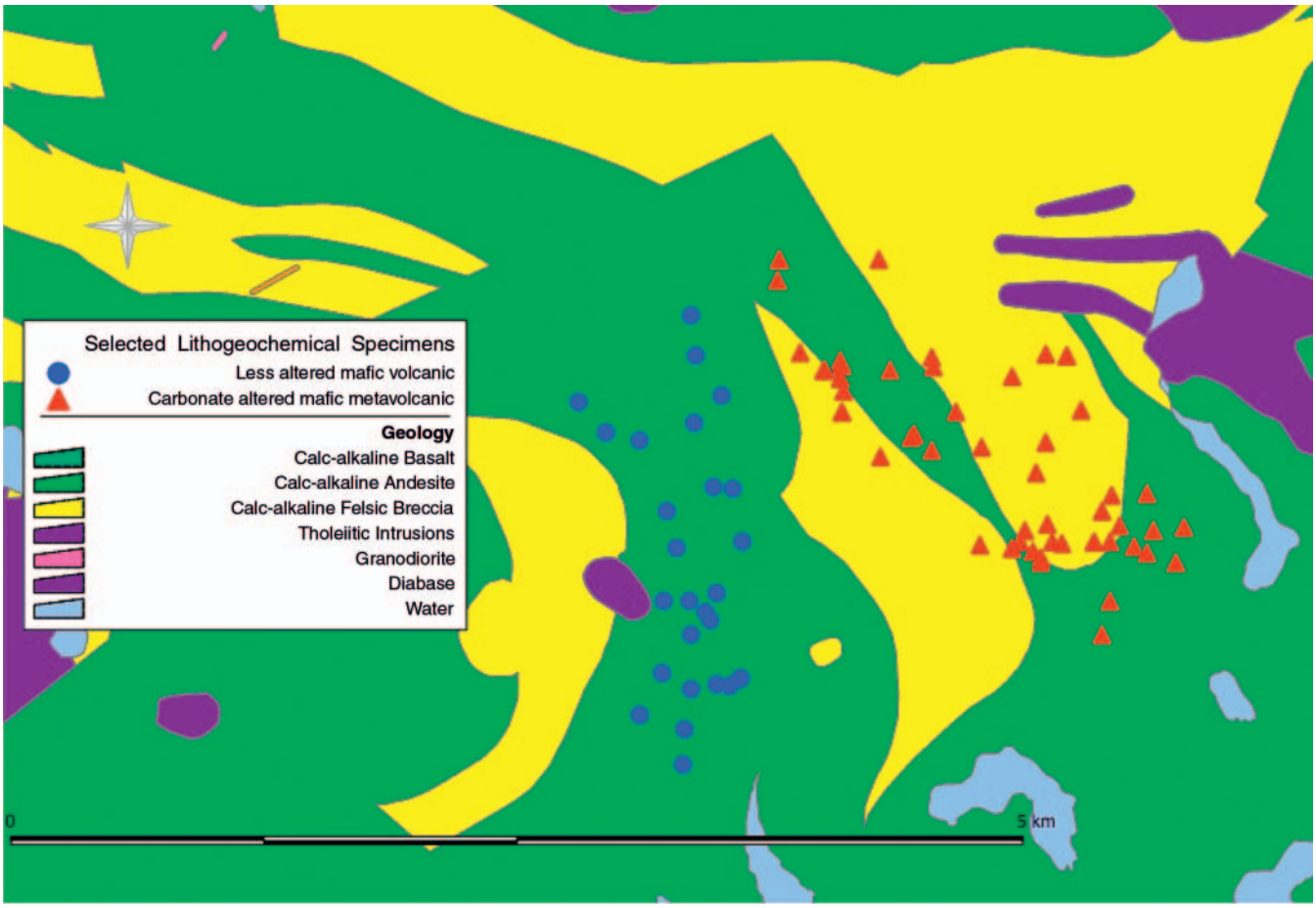


Plate 8. Map of altered/unaltered sampling sites in the Ben Nevis Township area.

Regional lake sediment surveys were carried out in five areas: Pancake Lake, Trout Lake, Hanes Lake, Montreal River and Cow River. The sampling programme was carried out over several years and the methods of analysis were similar for all five datasets. However, a levelling problem does exist amongst the survey areas. The greatest difference

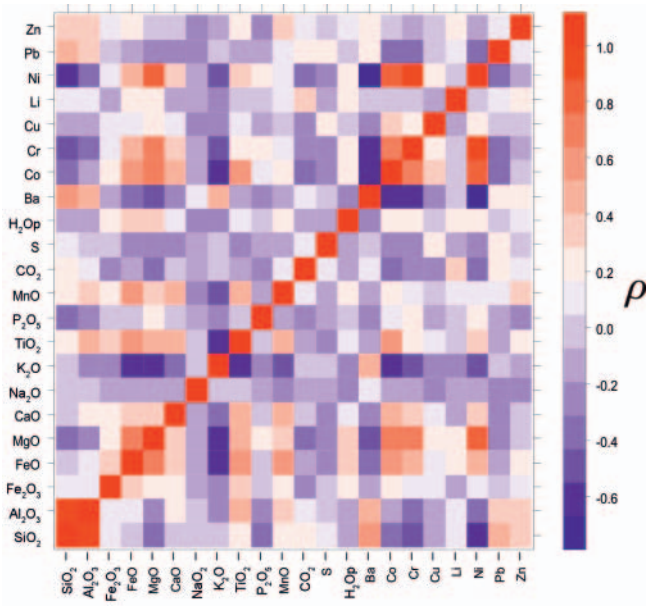
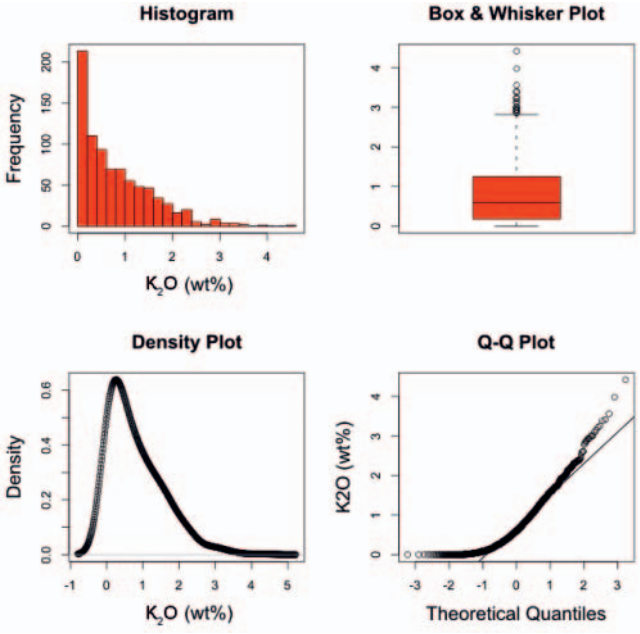


Plate 9. Correlation matrix expressed in terms of colour. The scale bar on the right of the matrix provides the measure of correlation based on colour.

between geochemical data exists between the Cow River map sheet and the adjacent Montreal River and Hanes Lake survey areas.

Figure 10 shows the range of values for Zn over the five areas in the Batchawana area. The interquartile range, shown in the solid box, is significantly higher for the Cow River data than for the other survey areas. However, the Cow River area also contains abundant mafic volcanic rocks of tholeiitic affinity that would naturally tend to have higher Zn values relative to the other survey areas which are composed of a mixture of tholeiitic and calc-alkaline volcanics, sediments and granitoid rocks. Plate 13 shows a map of Zn values throughout the region. The levels of Zn in the Cow River area (NE corner) are high relative to the other areas. There are a number of high Zn values within the centre of the volcanic sequence and these could be considered legitimate. However, the Cow River background Zn values appear to be 10–20 ppm higher than the background for the adjacent areas.

Using the approach outlined by Daneshfar & Cameron (1998), a quantile regression technique was applied. The procedure involves selecting 'bands' of specific distances (5, 10, 15, 20, 25 km, or some suitable scale depending on the nature of the surveys) between adjacent map sheets from which quantile regression is carried out for each of the bands. The



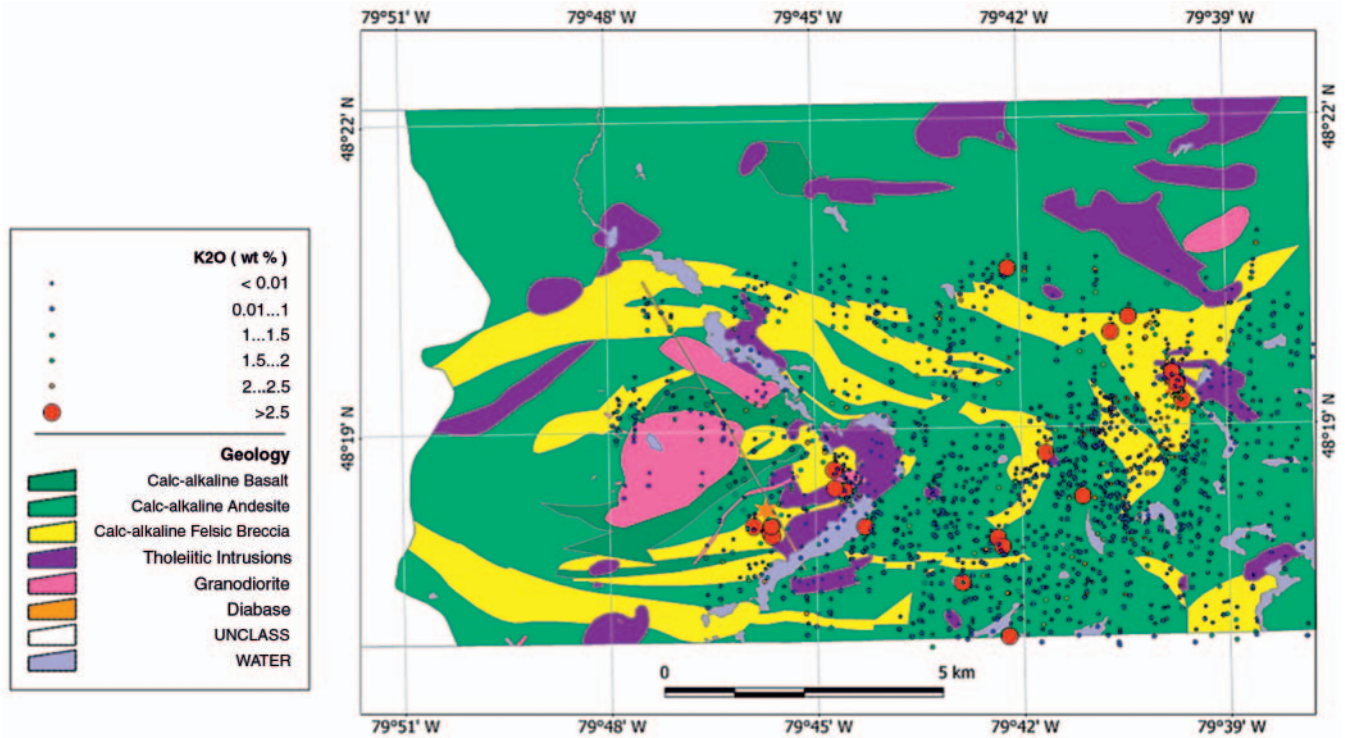


Plate 10. K_2O map across Ben Nevis Township. Separation of atypical K_2O values.

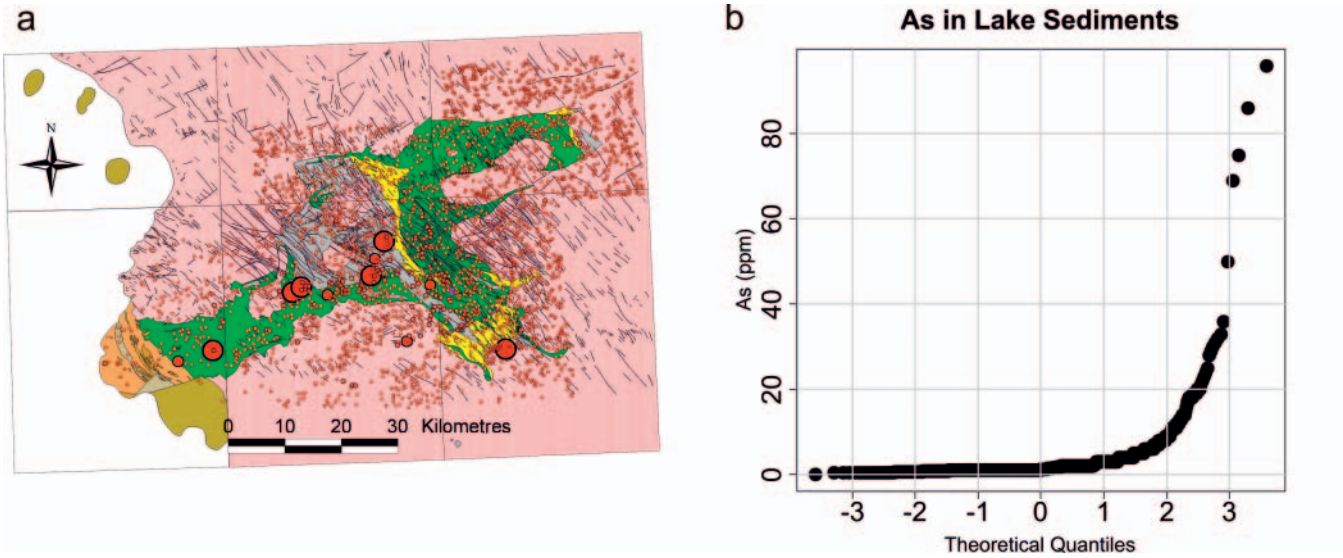


Plate 11. Map of atypical As (ppm) across the Batchawana area, Ontario.

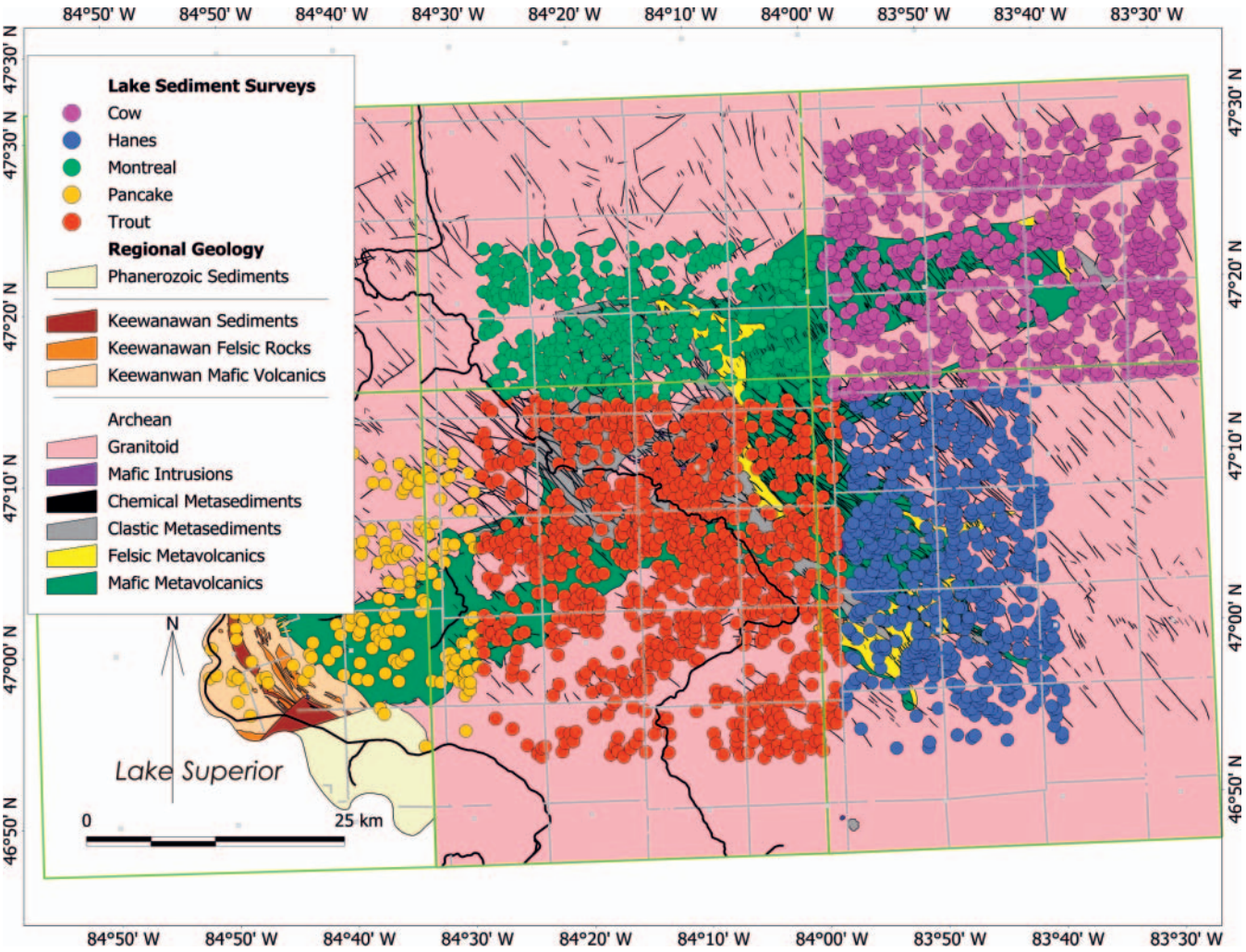


Plate 12. Lake sediment survey sites across the Batchawana area, Ontario.

reasoning for choosing bands is that an optimum distance, which results in the selection of an optimal number of specimens, will result in a best-fit quantile regression formula for levelling.

Plate 14 shows the selection of bands that were made for levelling the Cow River survey area against the Hanes Lake survey area. Bands were selected at the 5, 10, 15, 20 and 25 km ranges in a north–south direction.

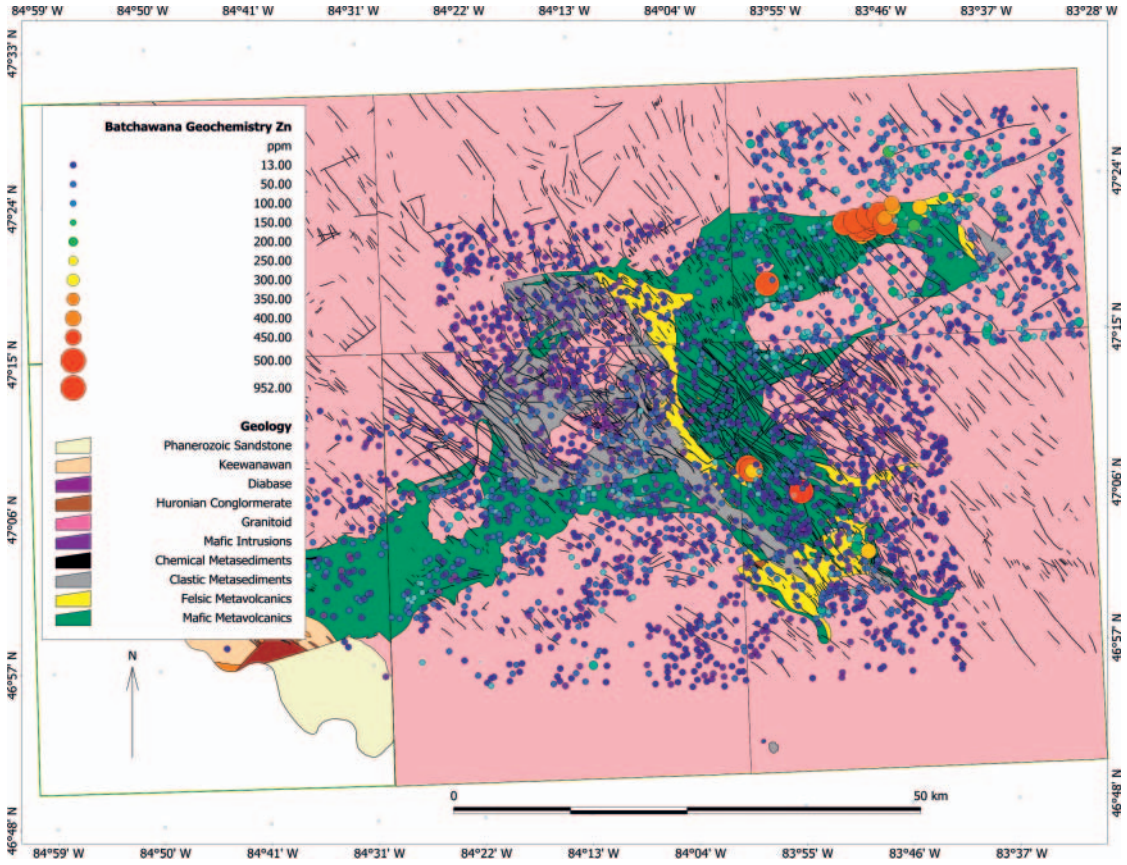


Plate 13. Unlevelled Zn values in lake sediments, Batchawana area, Ontario.

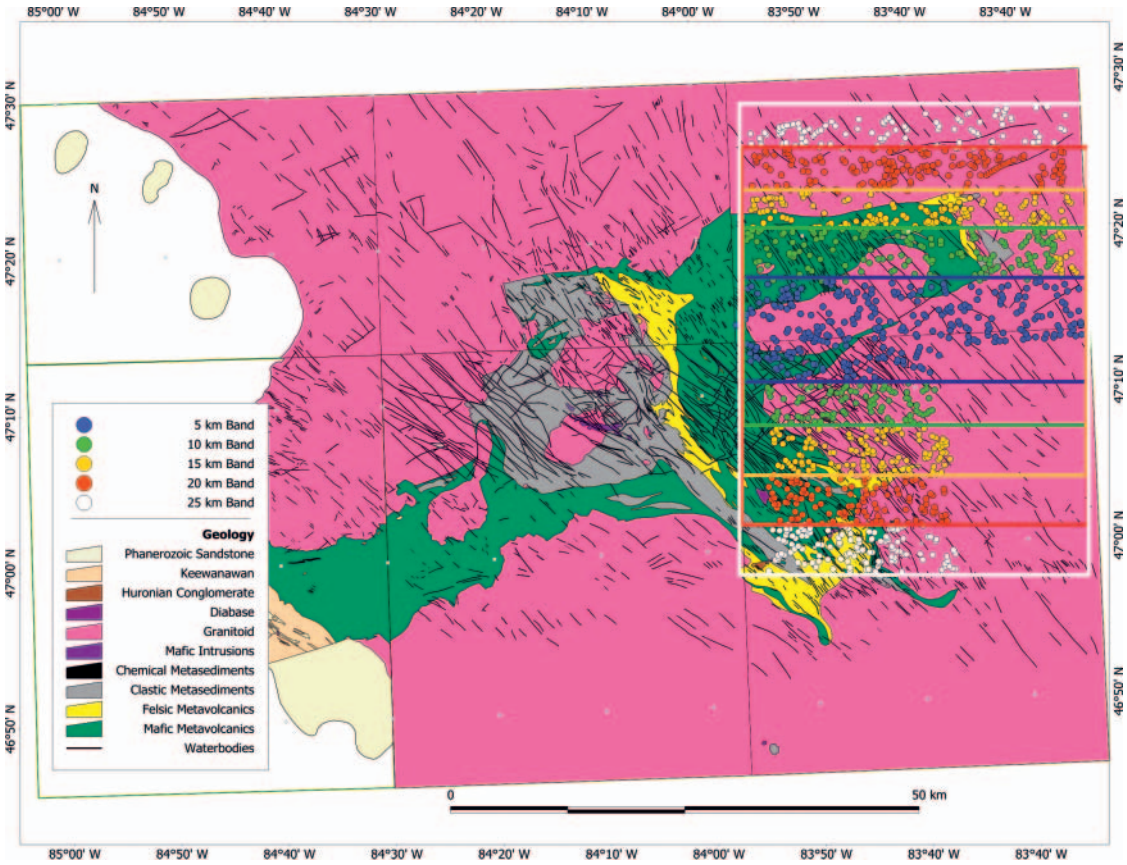


Plate 14. Band selection for quantile regression. Zn in lake sediments, Batchawana area, Ontario.

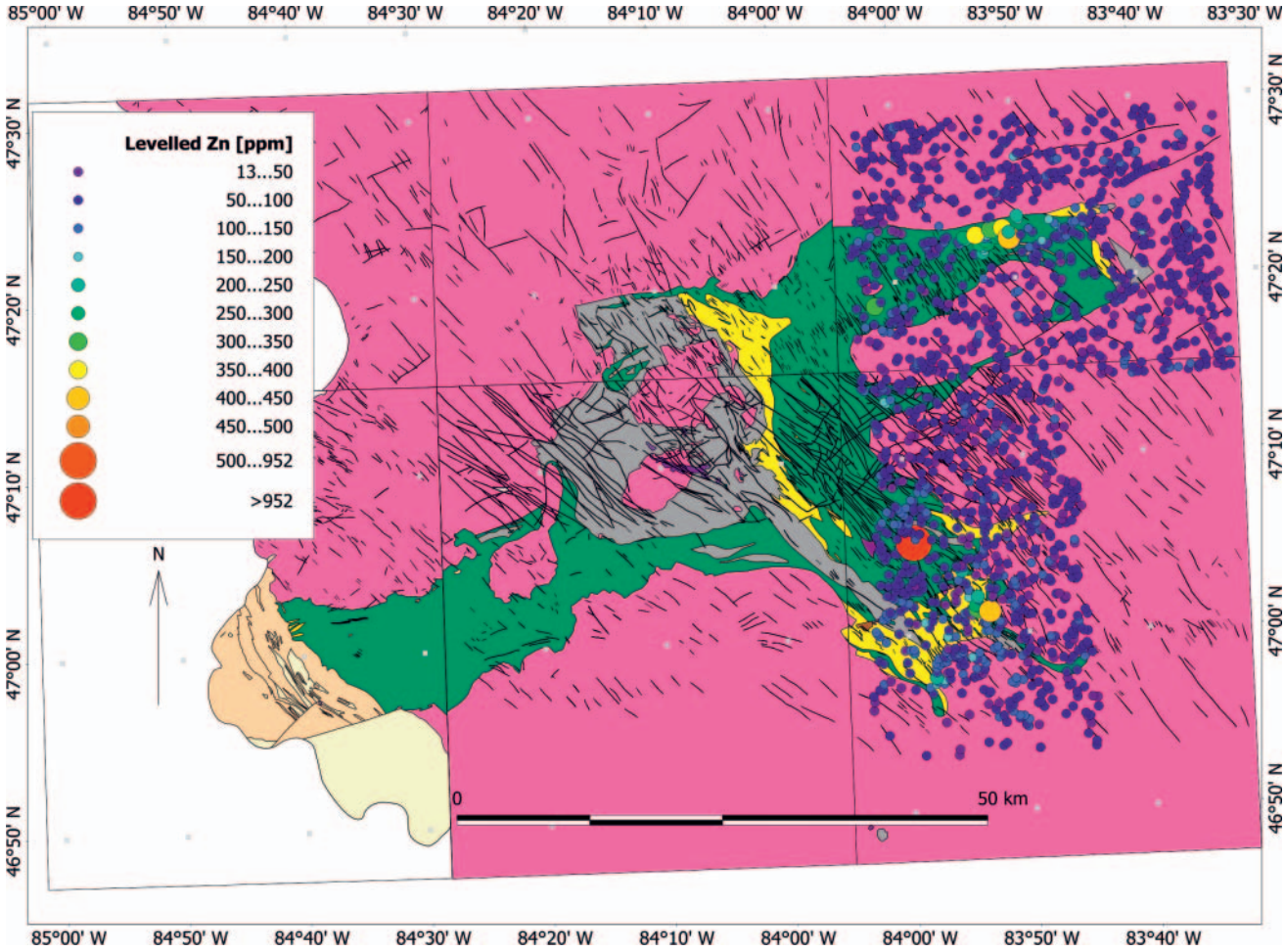


Plate 15. Levelled Zn values after applying quantile regression based on the 25 km band selection. See text for a detailed explanation.

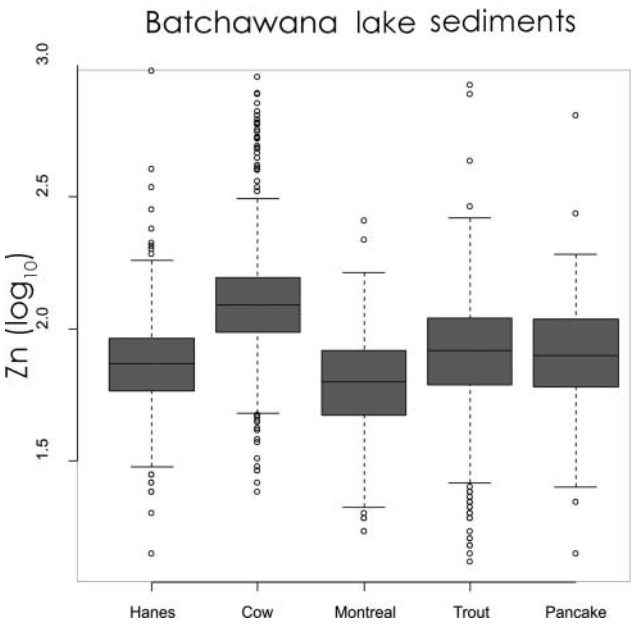


Fig. 10. Boxplots of Zn from the five survey areas, Batchawana area, Ontario.

For each of these bands, a linear regression was carried out. A measure, D, is used to determine which band provides the best quantile regression. D is defined as:

$$D = \sum w_i \left[(q_i)_e - (q_i)_{e'} \right]^2 \text{ where}$$

w_i is the assigned weight to the ith quantile,

$(q_i)_e$ is the ith quantile in band of width e

$(q_i)_e'$ is the ith quantile in band of width e' in the adjacent map sheet

e is the width of the band expressed as a measure of distance (i.e. m or km).

The weights favour quantile pairs at or near the median (50th percentile) of the distribution and are based on the ordinates of a normal distribution (weight for the median value = 0.399). These weights are listed in Table 2.

The work by Daneshfar & Cameron (1998) was originally carried out in British Columbia where the adjoining map sheets show broad geological similarity. When the same approach was tried in the Batchawana area the selection of bands of appropriate size became problematic.

Because of the deformed nature of the rocks and the subvertical stratigraphy, there is a significant variation in geochemical character over short distances. Figure 11a shows the results of the values of D applied to the five band selections and it is clear that the 5 km and 25 km bands have the lowest D values. The difference in D values for the different band selections is mostly due to the diversity of lithologies associated with each band. For the 5 km band, the lithologies are similar on both sides of the survey boundary: mafic volcanic and granitoid rocks. However, for the 10, 15 and 20 km bands, Plate 14 shows that there is a range of lithologies within the bands between the two surveys and the

Table 2. *Weights used for quantile regression in levelling geochemical data.*

Regression weights											
Quantile	5	10	20	30	40	50	60	70	80	90	95
Weight	0.103	0.175	0.28	0.348	0.386	0.399	0.386	0.348	0.28	0.175	0

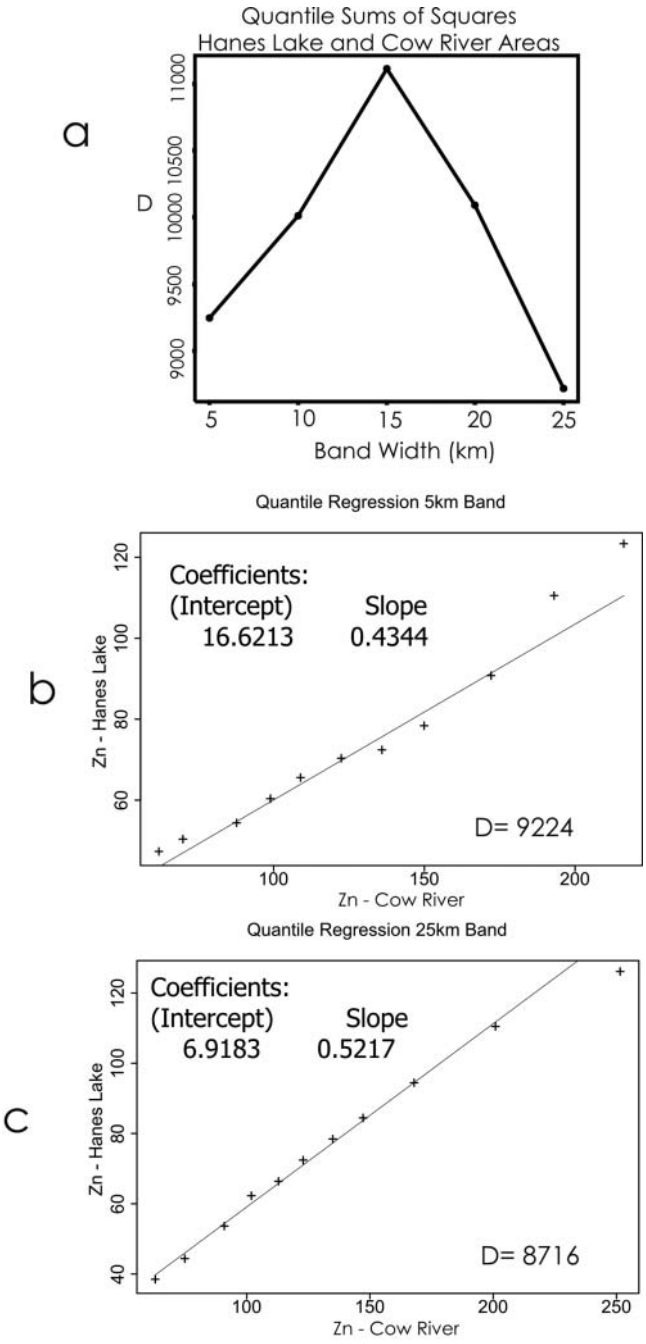


Fig. 11. Selection of optimum band width and quantile regression for Zn in lake sediments, Batchwawana area, Ontario.

lithologies are most dissimilar for the 15 km band. At the 25 km band, it is not surprising that the *D* value is lowest for the similar range of lithologies between the two survey areas and was thus the best band for the quantile regression methodology.

Quantile regressions were computed for both the 5 and 25 km bands (Fig. 11 b, c) using the weights for each quantile, which are shown in Table 2.

In Daneshfar & Cameron (1998) the weight for the 95th percentile was chosen as 0.103. For this application, many of the values for the Cow River Zn data were atypical and represented a group of specimens unique to Zn mineralization within the mafic volcanic sequence. There was no equivalent Zn response in the Hanes Lake survey area. Thus, the 95th percentile weight was changed from 0.103 to zero so that the effects of these large Zn values did not bias the levelling of the background.

The values of *D*, regression coefficients (intercept, slope) and plot of the quantiles for the 5 km band selection are shown in Figure 11b and for the 25 km band selection in Figure 11c. From the two plots, it can be seen that the 25 km band is a better fit and the results from this regression were used to adjust the Zn values in the Cow River survey area. Note that the results of this regression are equivalent to the shift and multiplier effect as shown in Figure 9d.

The results of applying the regression to the Cow River survey data for Zn are shown in Plate 15. The levelling procedure has had a significant effect on the lower values of Zn in the granitoid terrane but left the upper values, associated with the mafic volcanic rocks and some Zn rich zones within the volcanic sequence, relatively unaffected.

Levelling, using GIS and statistical procedures can produce an optimal result and a combination of these tools is a recommended way to level geochemical survey data.

MULTIVARIATE DATA ANALYSIS TECHNIQUES

Multivariate data analysis techniques such as PCA, cluster analysis, non-linear mapping and projection pursuit regression provide numerical and graphical means by which the relationships of a large number of elements and observations can be studied. These techniques typically simplify the variation and relationships of the data in a reduced number of dimensions, which may commonly be tied to specific geochemical/geological processes. The basics of multivariate data analysis techniques can be found in Jöreskog *et al.* (1976), Howarth & Sinding-Larsen (1983), Krzanowski (1988), Reyment & Jöreskog (1993) and Davis (2002). Mellinger (1987) provides a systematic approach to the application of multivariate methods in geological studies. Other methods include non-linear mapping (Sammon 1969), projection pursuit (Friedman 1987), multi-dimensional scaling (Kruskal 1964) and self-organizing maps (Kohonen 1995). A recent technique, independent components analysis (Comon 1994), is similar to the method of projection pursuit.

Incorporation of the spatial association with multi-element geochemistry involves the computation of auto- and cross-correlograms or co-variograms. This field of study falls into the realm of geostatistics, which is not covered in this contribution. A number of texts are available that provide details on geostatistics (David 1977, 1988; Journel & Huijbregts 1978; Isaaks & Srivastava 1989).

Grunsky (1986*a*) employed the use of PCA and clustering methods to evaluate the lithogeochemistry of Archaean volcanic terrains from which a number of geological processes were inferred, ranging from primary compositional variation to alteration and associated mineralization. This is discussed in greater detail below.

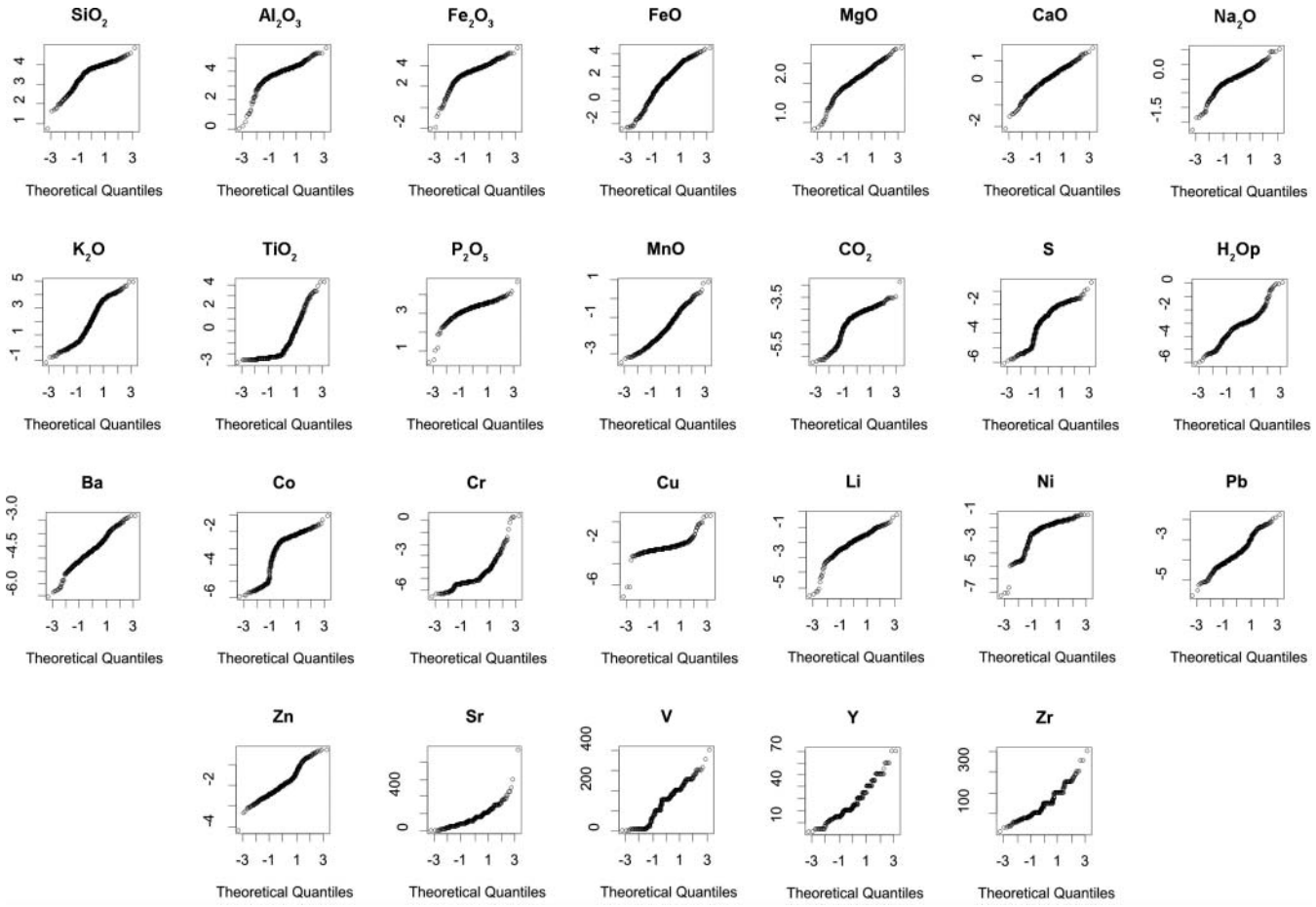


Fig. 12. Quantile–quantile plots of log-centred major and trace elements for the Ben Nevis lithogeochemical data.

Multivariate techniques that have been developed specifically for geochemistry include various empirical techniques such as the chalcophile and pegmatophile indices developed by Smith & Perdrix (1983), which were used to outline areas of potential base and precious metal mineralization in the Yilgarn craton of Western Australia.

Robust estimation of mean and covariance matrices

Many multivariate methods require estimates of correlation or covariance so that interrelationships between the variables can be quantified. Estimates of correlation/covariance are sensitive to the presence of outliers in the data that can bias the results. The influence of outliers can be reduced by applying robust methods to the estimation of the means, correlations and covariances between variables. In multivariate analysis, the distance of an observation to a centroid is estimated by the Mahalanobis distance which depends on an estimate of the multivariate mean and covariance. The Mahalanobis distance is defined as:

$$D^2 = [x - \bar{x}]' C^{-1} [x - \bar{x}]$$

where:

x is a vector of variables for a given observations;

$\bar{x}$ is a vector of the group mean;

C^{-1} is the inverse of the covariance matrix.

There are many techniques for determining robust estimates of mean and variances for individual populations (Rock 1987, 1988). Robust estimates can be determined for each individual variable or simultaneously for all variables. Multivariate estimates are affected by observations with missing values (no value) in any one of the individual variables. These must be discarded or have some suitable replacement value. Additionally observations that are censored (less than the detection limit) must have a proper replacement value as discussed previously. Campbell (1980) gave some early insight into the application of robust procedures in multivariate analysis. Venables & Ripley (2002, p. 336) provided a good discussion on robust estimation methods.

Two methods can be used to obtain robust multivariate estimates of means and covariance:

1. *Minimum Volume Ellipsoid (MVE)*. A multivariate method of determining means and correlations/covariances with minimal effect from outliers based on finding a hyperellipsoid that contains a subset of 'good' observations that minimize the volume of the ellipsoid. A geochemical application of this method is given by Chork (1990).
2. *Minimum Covariance Determinant* (MCD) *Estimatio*. This method works by minimizing the determinant (a measure of ellipsoid volume) of the covariance matrix based on a symmetric Gaussian hyperellipsoid. The method is faster than the minimum volume ellipsoid but has a lower breakdown point (Rousseeuw & van Driessen 1999). The determinant is based on a minimum number of 'good' observations. As the determinant decreases, the dispersion of the ellipsoid decreases with a corresponding drop in the estimates of central values, resulting in a 'robust' estimate.

If there are many observations with values at the same detection limit, a condition of collinearity occurs, which has a direct effect on the covariance matrix. If there are too many identical observations, the method fails. However, by increasing

the number of observations, the methods will generate less robust estimates. In the case of non-normal skewed distributions, the means and covariances will be affected. This type of problem is typically encountered when a percentage of the observations have elements with abundances below the detection limit (censored data) and increases the likelihood of collinearity problems.

An example of applying multivariate robust estimates is shown in Table 3 where estimates of the mean for 12 elements are given for 825 lithogeochemical observations from the Ben Nevis Township lithogeochemical data set. In this table, only estimates of the mean are shown. Classical estimates of the mean, based on univariate statistics, multivariate classical estimate, minimum volume ellipsoid and minimum covariance determinant methods are shown. Compared with classical methods of estimation, the robust estimate tends to minimize the effect of those distributions that are skewed.

For the minimum covariance determinant method, two estimates are shown based on two groups of 'good' observations. The initial estimate for the MCD used 419 observations based on an initial starting formula of (825 observations + 12 variables + 1)/2. Because of the large number of observations with values at the detection limit, the initial MCD estimate was singular. The MCD was applied using 540 and 800 observations. Table 3 shows that as the number of 'good' observations increases, the mean value tends towards the standard estimate-where the effect of the long tailed skewed distribution increases the estimate of the mean for several elements.

PRINCIPAL COMPONENT ANALYSIS

The objective of Principal Component Analysis (PCA) is to reduce the number of variables necessary to describe the observed variation within a dataset. This is achieved by forming linear combinations of the variables (components) that describe the distribution of the data. These linear combinations are derived from some measure of association (i.e. correlation or covariance matrix). Davis (2002, Chapter 6) gives a very readable account of the mathematics of PCA. More complete discussions on the theory and application of PCA can be found in in Jöreskog *et al.* (1976), Jolliffe (2002) and Jackson (2003). Appendix 2 provides a simple geometric description of PCA.

A method of PCA known as simultaneous RQ-mode principal component analysis (Zhou *et al.* 1983) has the advantage of presenting the principal component scores of the observations and the variables (elements) at the same scale, which permits plots of the observations and variables on the same diagram. This method is similar to the biplot method of Gabriel (1971). The interpretation of the results of PCA is usually oriented on placing a geological/geochemical interpretation on the linear combinations of elements (loadings) that comprise the components. This method has been implemented in the S programming language (Grunsky 2001).

Ideally, each principal component might be interpreted as describing a geological process such as differentiation (partial melting, crystal fractionation, etc.), alteration/mineralization (carbonatization, silicification, alkali depletion, metal associations and enrichments, etc.) and weathering processes (bedrock–saprolite–laterite). In lithogeochemical, weathered profile, lake sediment and stream sediment surveys, the first and second components commonly reveal relationships of observations and variables that reflect underlying lithological variation. In areas of thick overburden such as glacial till, alluvium or colluvium, the linear combinations of variables and the plots of the loadings may not be so easy to interpret as they may reflect a mixture of several surficial processes.

Maps of the principal component scores of the observations can be useful in understanding geochemical processes. If a component expresses underlying lithologies, then a map of that component will clearly outline the major lithological variation of the area. Components that outline other processes such as mineralization or alteration can also be expressed clearly on maps that display the component scores (e.g. Grunsky 1986*a*).

The measure of association, or metric, can have a significant effect on the derivation of principal components. Covariance relationships between the elements reflect the magnitude of the elements and thus elements with large values tend to dominate the variance–covariance matrix. This has the effect of increasing the significance of these elements in the results of the PCA. The correlation matrix represents the inter-element correlations, which is actually the standardized equivalent of the variance–covariance matrix. Other metrics of association can be used and this is discussed by Jöreskog *et al.* (1976) and Davis (2002). If the distributions of the elements are non-normal or there is a presence of outliers the estimates of correlation/covariance may be affected and it may be necessary to apply robust procedures (Zhou 1985, 1989).

In situations where there are outliers or atypical observations, or where the marginal distributions are not normal, a number of choices can be made:

1. If the marginal distribution is censored, find a suitable replacement value so that the mean and variance is a good estimate of the population mean and variance. This can be done by:
   a) assigning a replacement value that is *c.* ½ to ⅓ the censored value;
   b) using statistical procedures to estimate (impute) a replacement value based on the statistical characteristics of the uncensored portion of the data (i.e. the EM method) discussed previously.
2. If there are outliers present:
   a) remove the outliers from the calculation for means and covariances;
   b) apply robust procedures that minimize or eliminate the effect of these values.

Rare events, such as mineral occurrences or deposits, are usually under-represented in regional geochemical survey sampling schemes. A chemical signature that may be

Table 3. *Robust and non-robust estimates of central values, Ben Nevis Township lithogeochemistry.*

Method	Ba	Co	Cr	Cu	Li	Ni	Pb	Zn	Sr	V	Y	Zr
Univariate mean	208	23	83	56	17	78	17	89	135	132	24	132
Classical robust estimate	208	23	83	56	17	78	17	89	135	132	24	132
Univariate median	170	24	68	42	14	85	5	74	120	150	21	130
Minimum volume ellipsoid	194	22	81	38	15	78	7	73	140	139	26	138
Minimum covariance determinant 800 observations	207	23	84	47	17	79	10	78	136	133	24	132
Minimum covariance determinant 540 observations	198	22	82	39	15	79	6	73	140	139	25	136

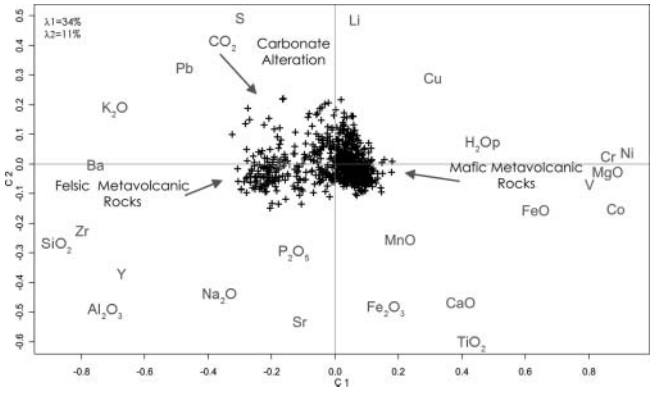


Fig. 13. Biplot of the first two principal components for the Ben Nevis lithogeochemical log-centred data.

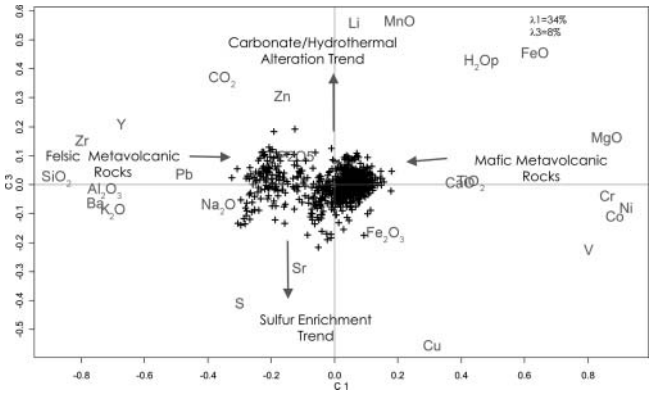


Fig. 14. Biplot of the first and third principal components for the Ben Nevis lithogeochemical log-centred data.

diagnostic of a unique geological event may show up as a linear combination of elements with a lesser principal component. Thus, it is important to scan all of the components to check for such features.

The following examples illustrate the use of PCA from the Ben Nevis metavolcanic data (see Plate 1). As it is a 'compositional' set of data, it sums to a constant (100%). The data were transformed using the logcentred transformation method described previously. The distributions for these transformed variables are shown in Figure 12.

The results of the PCA are shown in Table 4 where the eigenvalues, R-mode loadings, as well as the relative and actual contributions of the variables are presented. Results are shown for the first seven components only, which accounts for more than 72% of the variation in the data. The accompanying screenplot displays the successive eigenvalues for all of the components.

The R-mode loadings are the eigenvectors scaled by multiplying, in order, each of the eigenvectors by the square root of the eigenvalues. The first component accounts for 34% of the overall variation of the data as shown by the eigenvalues. The relative and actual contributions shown in Table 4 provide details on the relative significance of the variables. The relative contribution is the contribution that a variable makes over all of the components. The actual contribution is the contribution that a variable makes within a given component.

Biplots of PC1 v. PC2 and PC1 v. PC3 are shown in Figures 13 and 14, respectively. The scores of the observations are shown as crosses and the scores of the elements are shown as their name. Figure 13 (PC1 v. PC2) shows that the compositions of the mafic (Ni, Cr, Co, Mg, Fe) rocks plot on the positive side of PC1. Rocks reflecting felsic metavolcanic rocks (Si, Zr, Ba, K, Y, Al) plot on the negative side of PC1. Observations with relative enrichment in CO_2, S, Li, Pb and Cu, plot along the positive side of the C2 axis. Figure 14 is a biplot of the first and third components where samples with relative enrichment in S and Cu plot along the negative side of the PC3 axis.

Examination of the relative contributions for the first component shows that elements such as Si, Al, Mg, K, Ba, Co, Cr, Ni, V and Zr are accounted for primarily by this component. The actual contribution shows that the variation is spread almost equally amongst Si, Mg, K, Ba, Co, Cr, Ni, V and Zr within the first component (see Table 4). The relative contributions of the second component suggests alteration of the volcanic rocks with high loadings for CO_2, S, Li, Sr, Ti, Na, Ca, Fe^{3+} and Al. The relative contributions of the third component suggest alteration associated with more mafic rocks as indicated by Fe^{2+}, Mn, CO_2, S, H_2O^+, Cu and Li.

The Q-mode scores were interpolated to a 100 m resolution grid by kriging. Plate 16 shows an interpolated image of the first principal component. The distinction between the mafic and felsic volcanic rocks is evident by the colour map of the image. Green and blue areas are associated with felsic rocks and red to yellow areas are associated with mafic rocks as shown in the relationships of the observations and elements in Figure 13.

Plate 17 shows an image of the second principal component, which accounts for 11% of the variation in the data. The plot of PC1 v. PC2 in Figure 13 shows that the second component has Cu, Li, S, Pb and CO_2 associated with positive values of PC2. The image of Plate 17 shows that areas in red–yellow correspond to the zones of carbonate alteration and mineralization that are present around the Canagau Mines deposit and the Croxall property.

Plate 18 is an image of the third principal component (7.8% of the variation in the data). Areas associated with S and Cu enrichment are evident, most notably around the Canagau Mines Cu–Au deposit in the eastern part of the image. These areas are also adjacent to areas of CO_2, Li, and Zn enrichment, which represent altered and mineralized country rocks that surround the S–Cu zones of relative enrichment. Figure 14 shows that positive values correspond with areas of increased CO_2, Li, and Zn enrichment and negative values with S and Cu enrichment.

Much more information can be obtained by examining all of the principal components. Other components exhibit zoning of Ca around the main zone of carbonate alteration and K has an association with S at the mineral occurrences. The fourth component highlights the relationship between Zn and S at both the Canagau and Croxall properties. However, the illustration of the first three components shows that PCA is an effective method for exploring the structure of the geochemical data and assisting in deriving models of geochemical processes by the use of graphics and geographic representation.

PCA has many different uses in evaluating geochemical data, including the development of empirical indices for specific element targeting (see sections on Empirical indices and Weighted sums).

CLUSTER ANALYSIS METHODS

Cluster analysis methods are useful as an exploratory tool for detecting groups of multi-element data that may not be readily observable in simple scatter plots or through the use of methods such as PCA. The main objective of clustering algorithms is to identify distinct natural groupings within multi-dimensional data. Clustering methods can be broadly divided into hierarchical and non-hierarchical methods. The

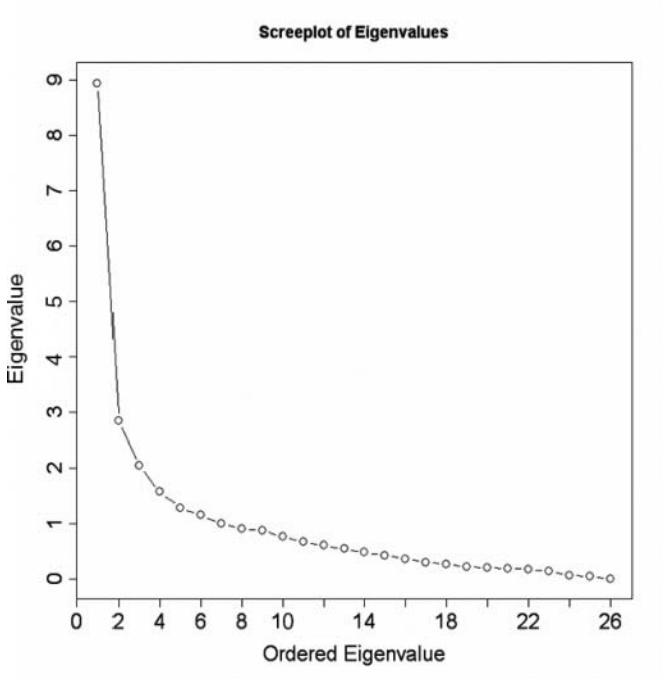
Table 4. *Principal components analysis of Ben Nevis lithogeochemical data. Analysis carried out on log-centred data.*

Eigenvalue

	PC1	PC2	PC3	PC4	PC5	PC6	PC7
λ	8.93	2.86	2.03	1.56	1.28	1.15	0.99
%	34.38	11.00	7.83	6.03	4.94	4.41	3.80
∑%	34.38	45.38	53.22	59.24	64.18	68.59	72.39

R-Loadings values <0 in italics

	PC1	PC2	PC3	PC4	PC5	PC6	PC7
SiO_2	*−0.87*	*−0.26*	0.03	*−0.06*	0.04	*−0.06*	0.11
Al_2O_3	*−0.72*	*−0.48*	*−0.01*	*−0.07*	0.18	*−0.15*	0.18
Fe_2O_3	0.17	*−0.48*	*−0.16*	*−0.55*	−0.01	*−0.06*	0.18
FeO	0.63	*−0.15*	0.46	*−0.25*	−0.03	0.03	0.11
MgO	0.86	*−0.03*	0.16	*−0.09*	0.19	0.14	0.02
CaO	0.40	*−0.47*	0.01	0.40	*−0.25*	*−0.28*	0.10
Na_2O	*−0.36*	*−0.44*	*−0.06*	0.40	0.15	0.15	0.04
K_2O	*−0.69*	0.19	*−0.08*	*−0.03*	0.34	*−0.16*	*−0.27*
TiO_2	0.43	*−0.60*	0.02	*−0.12*	0.02	*−0.14*	*−0.08*
P_2O_5	*−0.12*	*−0.29*	0.10	*−0.01*	*−0.14*	0.79	−0.24
MnO	0.20	*−0.25*	0.57	*−0.01*	*−0.47*	*−0.31*	−0.07
CO_2	*−0.35*	0.42	0.37	0.51	*−0.24*	*−0.16*	0.02
S	*−0.30*	0.49	*−0.41*	*−0.28*	*−0.37*	0.07	0.07
H_2O_p	0.47	0.07	0.43	*−0.38*	0.27	*−0.03*	0.30
Ba	*−0.76*	*0.00*	*−0.06*	*−0.03*	0.39	*−0.16*	*−0.20*
Co	0.88	*−0.15*	*−0.11*	0.03	0.05	*−0.04*	*−0.05*
Cr	0.86	0.03	*−0.03*	0.12	*−0.02*	0.20	*−0.11*
Cu	0.31	0.29	*−0.55*	*−0.24*	*−0.18*	*−0.15*	0.04
Li	0.06	0.49	0.56	0.10	0.39	0.09	0.20
Ni	0.92	0.04	*−0.08*	0.10	0.07	0.08	*−0.05*
Pb	*−0.47*	0.33	0.04	*−0.17*	*−0.14*	0.12	0.44
Zn	*−0.16*	0.01	0.31	*−0.40*	0.02	*−0.16*	*−0.55*
Sr	*−0.11*	*−0.53*	*−0.28*	0.21	0.21	0.05	0.24
V	0.80	*−0.07*	*−0.22*	0.04	0.13	*−0.13*	*−0.07*
Y	*−0.67*	*−0.37*	0.21	*−0.13*	*−0.27*	0.13	*−0.02*
Zr	*−0.80*	*−0.22*	0.16	*−0.13*	*−0.09*	0.13	0.00



Relative Contributions — values <10 in italics

	PC1	PC2	PC3	PC4	PC5	PC6	PC7
SiO_2	76.63	*6.93*	*0.11*	*0.42*	*0.16*	*0.38*	*1.13*
Al_2O_3	51.37	23.50	*0.01*	*0.46*	*3.28*	*2.32*	*3.21*
Fe_2O_3	*2.82*	22.97	*2.57*	30.83	*0.02*	*0.41*	*3.21*
FeO	40.09	*2.39*	20.99	*6.04*	*0.10*	*0.08*	*1.23*
MgO	74.13	*0.08*	*2.57*	*0.85*	*3.52*	*1.92*	*0.05*
CaO	15.68	21.67	*0.01*	16.36	*6.45*	*8.04*	*0.94*
Na_2O	13.08	18.99	*0.42*	16.27	*2.17*	*2.15*	*0.19*
K_2O	48.18	*3.78*	*0.66*	*0.09*	11.60	*2.44*	*7.38*
TiO_2	18.84	35.64	*0.03*	*1.51*	*0.05*	*1.87*	*0.60*
P_2O_5	*1.53*	*8.51*	*1.03*	*0.01*	*1.89*	62.58	*5.68*
MnO	*4.19*	*6.41*	32.38	*0.01*	22.15	*9.47*	*0.43*
CO_2	12.34	17.52	13.93	25.77	*5.67*	*2.47*	*0.05*
S	*8.95*	24.51	16.44	*7.59*	13.50	*0.43*	*0.54*
H_2O_p	21.91	*0.53*	18.59	14.41	*7.24*	*0.07*	*8.99*
Ba	57.25	*0.00*	*0.37*	*0.09*	15.04	*2.67*	*3.82*
Co	78.41	*2.27*	*1.10*	*0.06*	*0.24*	*0.14*	*0.24*
Cr	74.12	*0.08*	*0.12*	*1.35*	*0.04*	*4.06*	*1.18*
Cu	*9.44*	*8.52*	30.45	*6.00*	*3.17*	*2.19*	*0.15*
Li	*0.38*	23.88	31.60	*0.97*	15.43	*0.79*	*4.04*
Ni	84.74	*0.16*	*0.59*	*1.07*	*0.55*	*0.66*	*0.25*
Pb	22.52	10.69	*0.16*	*2.75*	*1.99*	*1.50*	18.97
Zn	*2.69*	*0.00*	*9.60*	15.86	*0.05*	*2.66*	30.15
Sr	*1.24*	27.99	*8.04*	*4.41*	*4.47*	*0.27*	*5.80*
V	64.40	*0.46*	*4.92*	*0.18*	*1.60*	*1.61*	*0.54*
Y	45.31	13.64	*4.50*	*1.62*	*7.16*	*1.74*	*0.04*
Zr	63.61	*4.98*	*2.45*	*1.69*	*0.85*	*1.80*	*0.00*

Actual Contributions — values <10 in italics

	PC1	PC2	PC3	PC4	PC5	PC6	PC7
SiO_2	*8.57*	*2.42*	*0.05*	*0.27*	*0.12*	*0.33*	1.15
Al_2O_3	*5.75*	*8.21*	*0.00*	*0.29*	*2.56*	*2.02*	3.25
Fe_2O_3	*0.32*	*8.03*	*1.26*	19.68	*0.02*	*0.36*	3.24
FeO	*4.48*	*0.84*	10.31	*3.86*	*0.08*	*0.07*	1.25
MgO	*8.29*	*0.03*	*1.26*	*0.54*	*2.74*	*1.67*	0.05
CaO	*1.75*	*7.57*	*0.01*	10.44	*5.02*	*7.01*	0.95
Na_2O	*1.46*	*6.64*	*0.21*	10.39	*1.69*	*1.87*	0.19
K_2O	*5.39*	*1.32*	*0.32*	*0.05*	*9.04*	*2.13*	7.47
TiO_2	*2.11*	12.46	*0.01*	*0.96*	*0.04*	*1.63*	0.61
P_2O_5	*0.17*	*2.97*	*0.51*	*0.01*	*1.47*	54.55	5.75
MnO	*0.47*	*2.24*	15.90	*0.01*	17.25	*8.25*	0.44
CO_2	*1.38*	*6.12*	*6.84*	16.45	*4.42*	*2.15*	0.05
S	*1.00*	*8.57*	*8.07*	*4.84*	10.52	*0.38*	0.55
H_2O_p	*2.45*	*0.19*	*9.13*	*9.20*	*5.64*	*0.06*	9.10
Ba	*6.41*	*0.00*	*0.18*	*0.06*	11.71	*2.33*	3.86
Co	*8.77*	*0.79*	*0.54*	*0.04*	*0.19*	*0.12*	0.24
Cr	*8.29*	*0.03*	*0.06*	*0.86*	*0.03*	*3.54*	1.20
Cu	*1.06*	*2.98*	14.95	*3.83*	*2.47*	*1.91*	0.15
Li	*0.04*	*8.35*	15.52	*0.62*	12.02	*0.69*	4.08
Ni	*9.48*	*0.05*	*0.29*	*0.68*	*0.43*	*0.58*	0.26
Pb	*2.52*	*3.74*	*0.08*	*1.75*	*1.55*	*1.31*	19.20
Zn	*0.30*	*0.00*	*4.72*	10.13	*0.04*	*2.32*	30.52
Sr	*0.14*	*9.78*	*3.95*	*2.81*	*3.48*	*0.24*	5.87
V	*7.20*	*0.16*	*2.42*	*0.12*	*1.24*	*1.40*	0.55
Y	*5.07*	*4.77*	*2.21*	*1.03*	*5.58*	*1.52*	0.04
Zr	*7.12*	*1.74*	*1.20*	*1.08*	*0.66*	*1.57*	0.00

following example shows the use of k-means clustering as a method for partitioning multivariate geochemical data. Davis (2002) is a good introductory review of clustering methods; Sinding-Larsen (1975) used clustering methods for the initial subdivision of a heterogeneous geochemical area; Jaquet *et al.* (1975) gave a detailed analysis of lake sediment geochemistry using clustering procedures; Howarth & Sinding-Larsen (1983) provided a general discussion of clustering methods applied to geochemical exploration; and Grunsky (1986*a*) has shown how dynamic cluster analysis (Diday 1973) was used to detect different types of mineralization based on distinct geochemical differences between the mineral occurrences. The use of fuzzy clustering methods in geochemistry was introduced (Bochang & Xuejing 1985).

Hierarchical clustering is based on the linking of variables (R-mode) or observations (Q-mode) through measures of similarity. The relationships between the variables or observations can be graphically expressed using a dendrogram. Individual clusters can be discriminated by choosing an appropriate value of linkage, which separates internally similar groups of objects into dissimilar groups. Hierarchical clustering assumes that all variables are linked at some level, which may not be a reasonable assumption in some instances.

The correlation coefficient (R-mode) is the most common measure of similarity for clustering. For Q-mode analysis (similarities between the observations), the Euclidean distance can be used as a measure of proximity by which observations can be clustered. However, when the number of observations is large the computation becomes intractable.

Arbitrary origin methods are non-hierarchical and may offer some advantage over hierarchical methods since the clusters are formed based on multivariate similarities (proximities) rather than individual correlation coefficients. These methods start with an initial number of cluster centres that can be specified or randomly chosen. Each observation is allocated to one of the groups based on proximity to the group centres. The process is iterative and group centres change until a stable solution results. Methods such as K-means (McQueen 1967; Everitt 1974; Hartigan 1975) or dynamic cluster analysis (Diday 1973) are examples of these techniques. Kaufman & Rousseeuw (1990) also describe a number of clustering methods.

K-means clustering

K-means cluster analysis is a method that starts with an initial 'guess' of the cluster centres. The distance of each observation from each cluster centre is measured and then provisionally assigned to the closest cluster centre. A new cluster centre is calculated based on the designated observations for each previous centre. The process is iterative until it converges on stable centres. The method requires an initial choice of the number of cluster centres. If the number is too great, there will be many small clusters that have few points. If the number of centres is too few, then the structure of the data may not be realized. A disadvantage of the procedure is that a less than optimal clustering may result if the initial cluster centres do not fall in distinct clusters (Davis 2002, p. 500). Venables & Ripley (2002) provide a method by which a suitable number of starting clusters may be determined by using a combination of hierarchical clustering and PCA.

It is common to apply non-hierarchical clustering methods to principal component scores. If one or more principal components can be inferred to represent specific geological/geochemical processes, then the application of cluster analysis can provide further insight in how those processes may be related. Additionally, the component plots provide a reduced set of dimensions for viewing the multi-element associations of the data and thus provide additional visual assistance in examining grouped associations.

K-means clustering was applied to the logcentred transformed Ben Nevis township metavolcanic data. The number of clusters was set at 10, based on the perceived variation in the rock types (felsic metavolcanics, mafic volcanics, mafic intrusions, granite) as well as the two known mineralization zones that have surrounding alteration. The results of the clustering are shown in Plate 19. Each observation is labelled with the group number to which it was assigned. Several clusters (Groups 1, 2, 5, 6, 8 and 10) are associated with the distinctions between mafic and felsic metavolcanic rocks. Groups 3 and 9 are directly associated with mineralization. Observations that belong to these groups occur where there is known mineralization. There are also two clusters associated with carbonate alteration (Groups 4 and 7), which occur in the eastern part of the map area. It is apparent that the observations assigned to each group not only share similar geochemical characteristics but also have close spatial associations, as shown in Plate 19.

Multivariate ranking using the Mahalanobis distance: a multivariate extension of Q–Q plots

The use of the covariance matrix as a tool for distinguishing background from anomalous populations is well established in geochemical research (Garrett 1989*c*, 1990; Chork 1990). Filzmoser *et al.* (2005) have written a library of routines ('*mvoutlier*') that is available as part of the R environment (www.r-project.org/cran). The covariance matrix contains information on the variability of the elements as well as their inter-relationships. The multi-element data constitute a hyper-ellipsoid in multi-dimensional space. The mean value of each element defines the centroid of this hyper-ellipsoid and the distance from each observation point to the centroid is the Mahalanobis distance. In a multivariate normal population, most observations lie within an expected radius of the centroid, which defines the background group of observations. However, if outliers are included in the data, the shape of the hyper-ellipsoid will change. This resulting distortion affects the location of the centroid and thus affects the Mahalanobis distance for all of the observations. In such cases, the application of robust procedures is recommended.

Outliers can be distinguished from the main background population by determining the Mahalanobis distance of each observation from the group centroid. The distances can be compared to the 'expected' distances of a multivariate normal population (cumulative probability with the number of degrees of freedom defined as the number of variables) by the use of χ^2 values as defined by Garrett (1989*c*). If the population is multivariate normal, then the plotted pairs form a straight line. If the population contains outliers, then the observed Mahalanobis distances (D^2) are greater than the expected χ^2 quantiles and the plot becomes non-linear. However, the χ^2 distribution is long-tailed near the extreme ends of the distribution and this property may mask outliers with large Mahalanobis distances. An alternative to the use of the χ^2 values is the cubed root of a normal distribution, which does not have the long tail property of the χ^2 distribution and is thus less likely to mask outliers.

The lake sediment survey data from the Batchawana area of Ontario were evaluated for the potential to host Cu, Zn and precious metal deposits. A suite of elements (Cu, Zn, As, Sb and W) was chosen to test the possibility that these elements could identify potential mineral deposits. For these data, censored values were replaced with estimates from the EM method for

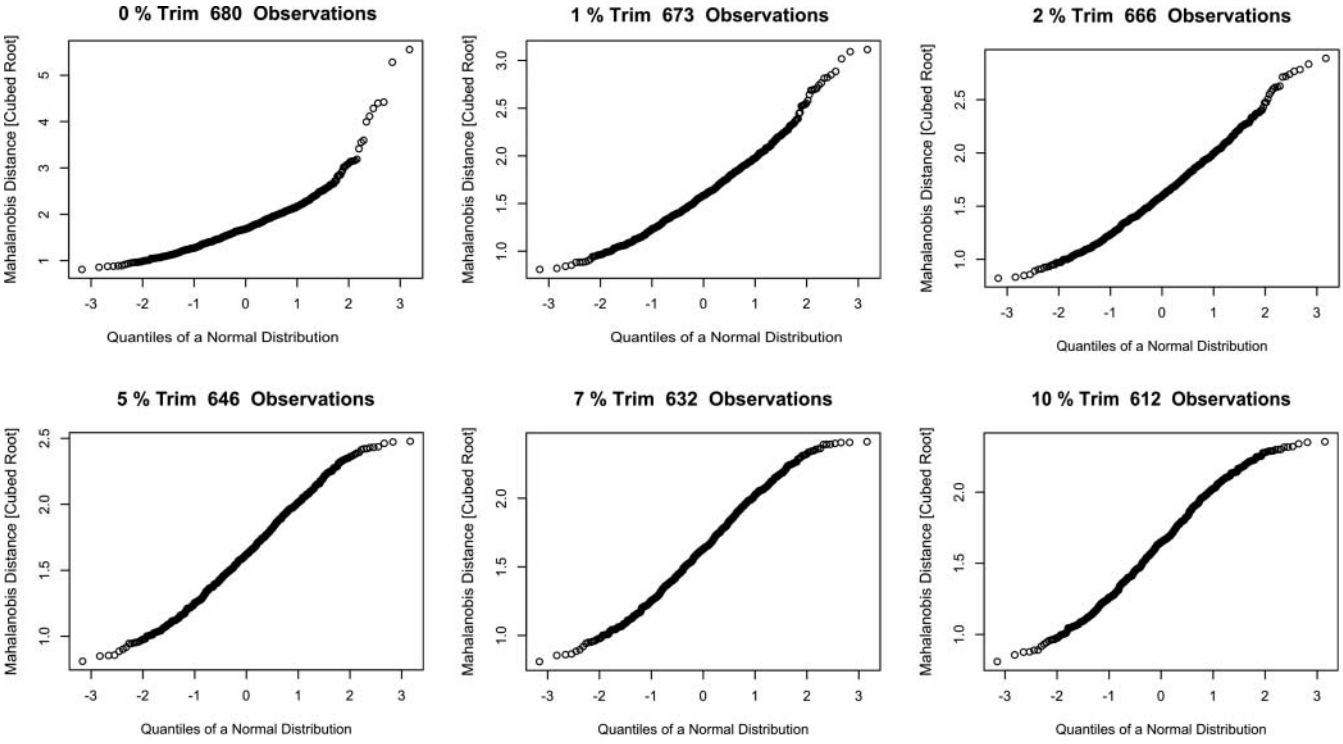


Fig. 15. Mahalanobis distance (D^2) plots of a multi-element suite (Cu, Zn, As, Sb, W) of lake sediment data. Successive trimming of the outliers defines a homogeneous background population. The deleted outliers are then follow-up for their potential as sites of mineralization.

determining replacement values for censored distributions. Because these data are compositional, they were normalized to a constant sum and then transformed using logratios.

Figure 15 shows a series of ranked Mahalanobis distance plots versus the cubed root of a normal distribution for different degrees of trimming. The first figure shows a plot of all of the observations. The plot displays a curved line with several outliers at the positive end of the curve, suggesting that there are observations which are not part of a multivariate normal population. Each successive plot is the data with the outliers from the previous plot removed. For each plot, a new centroid and corresponding Mahalanobis distances were re-computed. Trimming of the data in the 7% to 10% range yields a reasonably straight curve which suggests that the trimmed observations could be considered atypical and warrant further investigation.

The 10% of data that were trimmed data were then re-inserted into the data matrix from which the D^2 values were computed based on the covariance from the other 905 of the data. The ranked multivariate distance values are plotted on the map and graph in Plate 20. Observations with high D^2 values are locales of interest and warrant further investigation. Note that observations, which are atypical, are not necessarily geochemically 'anomalous'. No multivariate equivalent of a threshold was established, although the 10% trim could be used as an initial starting point in establishing the threshold.

The use of empirical indices

The existence of pathfinder elements has prompted the use of several numerical procedures through which selected elements can be used in an exploration programme by creating mineralization potential indices based on the weighted sum scores of the pathfinder elements. Empirical indices can be determined from selected elements that are associated with specified geochemical processes. The techniques used in this approach are described by Garrett *et al.* (1980), Chaffee (1983), Smith & Perdrix (1983), Smith *et al.* (1987) and Garrett (1991). Garrett & Grunsky (2001) have reviewed objective comparisons of various weighting schemes used to highlight observations defined by pathfinder elements.

In many geochemical studies, several pathfinder elements may be identified for defining target areas (mineralization, anthropogenic sources). These pathfinder elements may be chosen based on geological/geochemical knowledge of the processes of interest. Combining these pathfinder elements together through a multivariate ranking scheme is a potentially useful tool for defining multi-element anomalies. Defining the pathfinder elements can be based on geological knowledge or through the use of data analysis/discovery procedures discussed previously, such as PCA and cluster analysis. These methods can reveal relationships in the data that may be directly related to underlying lithologies or processes of interest (mineralization, anthropogenic effects) from which pathfinder elements can be determined.

Chaffee (1983) developed a method of scoring observations for anomaly potential. Each element is evaluated such that the range of values are subdivided into four groups, by thresholds, with corresponding scores that represent background (0), weakly anomalous (1), moderately anomalous (2), and strongly anomalous (3). These ranges are derived from orientation studies over areas where the range of values and underlying geochemical distributions are reasonably well understood. Each is then assessed with respect to each element. Observations with the highest scores are considered anomalous and are targeted for further follow-up.

Smith & Perdrix (1983), Smith *et al.* (1987) and Smith *et al.* (1989) made use of three indices derived from geochemical trends that were noted in the laterite geochemistry of the Yilgarn Block of Western Australia. A group of pathfinder elements, As, Sb, Bi, Mo, Ag, Sn, and W, form the basis of these empirical

indices known as CHI-6*X, NUMCHI, and PEG-4. These indices show elevated values of these pathfinder elements in lateritic materials associated with greenstone belts, shear zones, base metal and precious metal deposits (CHI-6*X and PEG-4). These indices are based on simple equations as follows.

The coefficients provide weighting to the elements such that observations with elevated chalcophile values have high CHI-6*X or PEG-4 indices. These coefficients were derived for lateritic materials only. The coefficients need to be altered for other materials. The CHI-6*X index is suited more to isolating observations with elements associated with precious metal deposits, whereas the PEG-4 index is suited for isolating observations with elements associated with pegmatophile environments, such as Sn deposits within granitoid terrains.

The NUMCHI index is a score of the number of elements that exceed the threshold for each element. Thus for a given specimen, if nine elements exceed their respective thresholds, then the NUMCHI index will have a value of 9. As discussed previously, threshold values are chosen from visual inspection of summary tables, order statistics, Q–Q plots etc.

Weighted sum index

Garrett *et al.* (1980, p.144) suggested the use of a linear combination of a group of indicator elements that give a weighted sum. In a multi-element survey, those elements which are considered pathfinders are given more weight than elements that may be more diagnostic of background. The choice of weights may be based on the knowledge of the investigator. Alternatively, principal component loadings may be used as a starting point. Examples of the use of this index are given by Garrett *et al.* (1980) and Garrett & Grunsky (2001).

INTEGRATION OF MULTI-ELEMENT GEOCHEMISTRY AND DIGITAL TOPOGRAPHY: AN EXAMPLE OF PROCESS IDENTIFICATION, INDONESIA

Modern methods of data management including the use of desktop database management systems (DBMS) combined with GIS that can produce images of multiple datasets simultaneously provide significant assistance in the management and presentation of geochemical data. In many areas of the world, digital base maps can be acquired from local governments that typically include lakes, rivers, streams, road networks and other topographic information that is useful in the orientation and interpretation of geochemical data. In addition, digital topographythat provides a topographic relief backdrop for the interpretation of geochemical data may also be available. Digital geological maps are now routinely provided by many geological surveys, together with mineral occurrence inventory databases that have been accumulated from both geological survey and private company data.

Digital topography offers a unique view of data in that it provides a 'real world view' of the data over the terrain. When digital air photos or satellite imagery are integrated with digital topography and viewed using image processing systems with three dimensional rendering ability, the viewer gets a sense of looking at the terrain from an aircraft. Interpolated geochemical images can generally be interpreted more effectively when merged with digital topography and viewed in a similar manner. Grunsky & Smee (1999) demonstrated the usefulness of integrating digital elevation data with multi-element geochemistry from a soil survey on the island of Sumatra in Indonesia. Cheng *et al.* (2000) also demonstrated the use of fractal methods for isolating the patterns associated with Cu enrichment in the area.

Difficulties were encountered when the interpretation of selected elements was attempted and the observed patterns appeared to be discontinuous and erratic. However, the application of multivariate statistical methods identified two distinct geochemical associations: recent volcanic ash, and a saprolitic soil profile containing a mineralized zone of Cu associated with mafic volcanic rocks. Plate 3 shows the soil sampling grid from which 1665 samples were collected and analysed for Au, Cu, Pb, Zn, As, Sb, Ba, Ca, Cd, Co, Cr, Fe, Ga, K, La, Li, Mg, Mn, Nb, Ni, Sc, Sr, Ti, V, Y, Zr, and Hg, using *aqua regia* digestion and ICP-ES.

The results of the application of a PCA applied to the logcentred data in which two distinct sample populations representing saprolite and ash and a trend of Cu enrichment associated with Cu mineralization are shown in Figure 16. The bi-modal population, seen along the C1 axis of the biplot represents material that is interpreted to be volcanic ash that overlies the saprolitic soils.

Plate 21 shows a draped image of the interpolated scores of the first principal component draped over a 25 m DEM, derived from the scores of population on the positive side of the C1 axis (Fig. 16). The elevation ranges from 1180–1350 m. Note that the cyan-green-yellow-red areas represent the interpolated positive scores of the first principal component. These areas have been interpreted to be volcanic ash occurring along hill tops and the eastern slopes of the hills. This interpretation is supported by observations of the sampled media and reports by geologists in Indonesia where this phenomenon is commonly observed. The second component draped over the DEM (Plate 22) represents the Cu-enrichment trend and is associated with mafic volcanic rocks trending northwesterly along the western slopes and coincident with the regional stratigraphy.

This example highlights the effective use of multivariate statistical methods for distinguishing between different sample media as well as the isolation of geochemical trends that define zones of possible mineralization. The use of these types of multivariate methods isolates relationships of the elements that are difficult or impossible to see by examining individual elements. The application of multivariate techniques integrated with digital elevation models provides a more effective way of visualizing and interpreting elemental data.

ANALYSING LARGE GEOCHEMICAL DATASETS: AN EXAMPLE FROM THE CAMPO MORADO DISTRICT, MEXICO

The Campo Morado mining camp in the Guerrero state of Mexico hosts seven precious metal-bearing volcanogenic massive sulphide deposits in the complexly folded and faulted Guerrero terrain (Oliver *et al.* 1996; Rebagliati 1999). Approximately 29 221 samples were collected over a soil grid comprising 25 m sample intervals along lines and spaced 100 m apart. The field samples were analysed for Al, Fe, Ca, K, Mg, Na, Ti, Au, Ag, As, Ba, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, P, Pb, Sc, Sr, V, W and Zn using *aqua regia* digestion and ICP-ES. A DEM was created at 25 m resolution. PCA was carried out on the data and revealed several significant patterns related to lithological variation and mineralization. Because of the high topographic relief in the area, the problem of transported material from weathering has the potential to result in false anomalies that are often due to hydromorphic dispersion and down-slope creep. When the results of the PCA are draped over the topography, there is an increased ability to distinguish anomalies associated with hydromorphic dispersion from those associated with a bedrock source.

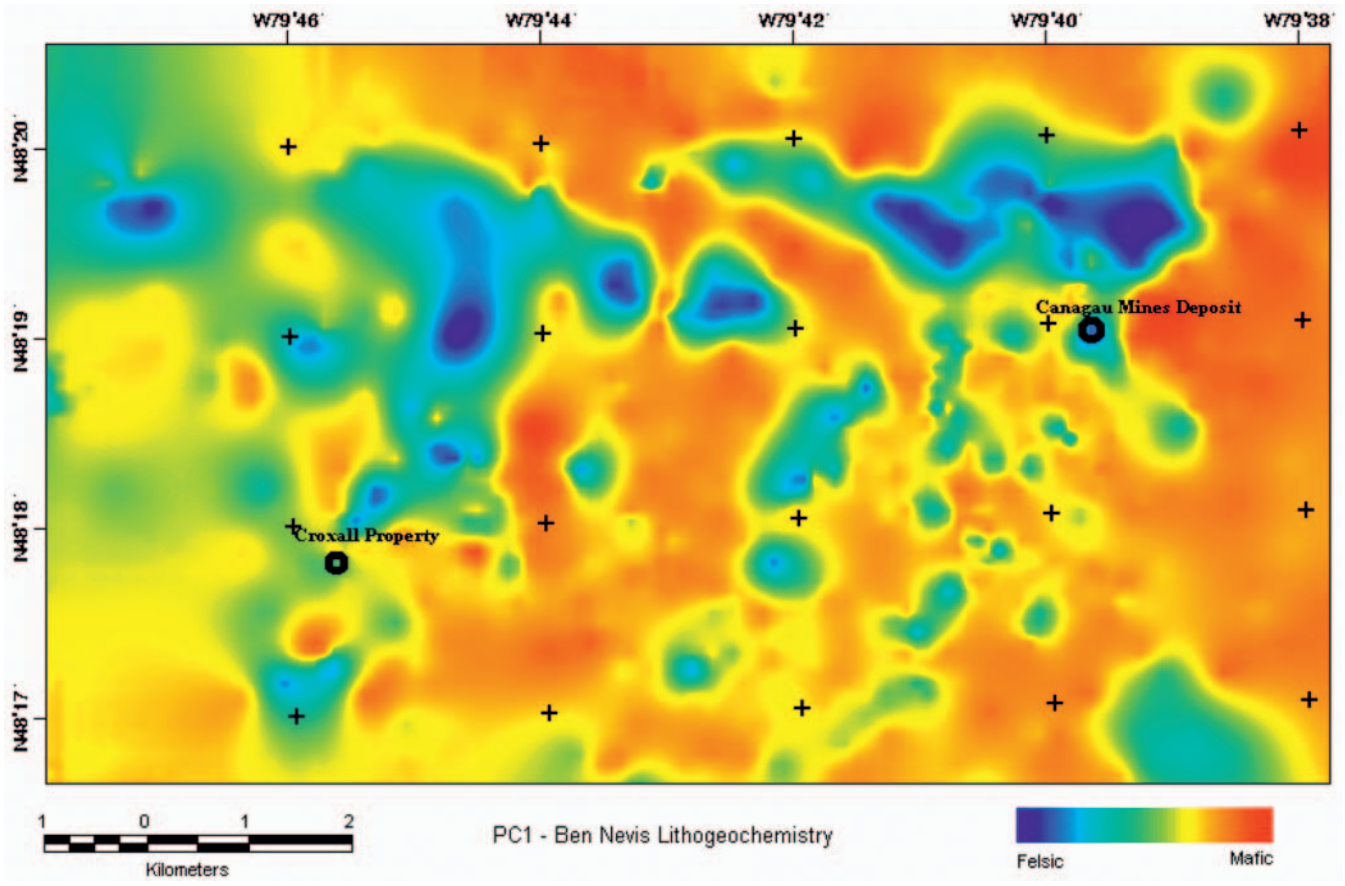


Plate 16. Image of the first principal component derived from the log-centred lithogeochemical data, Ben Nevis Township, Ontario. This image outlines the lithological variation.

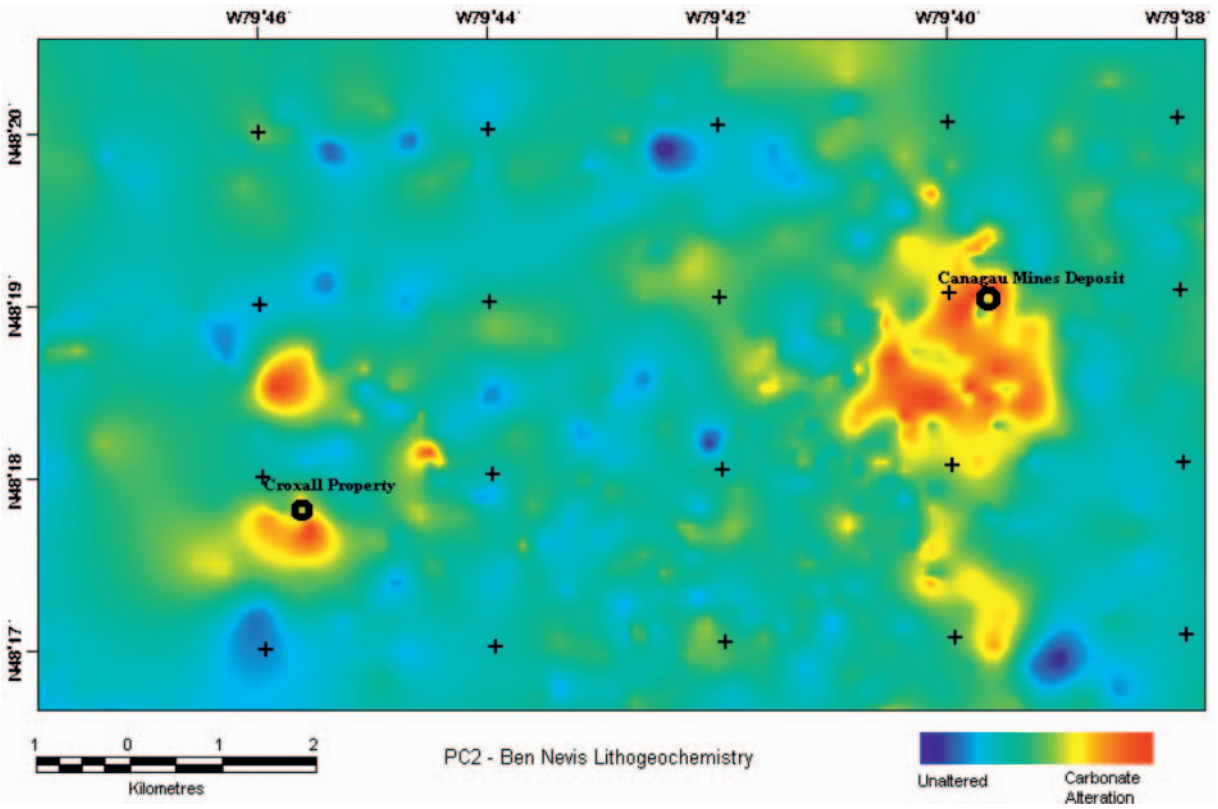


Plate 17. Image of the second principal component derived from the log-centred lithogeochemical data, Ben Nevis Township, Ontario. This image outlines the zones of carbonatization.

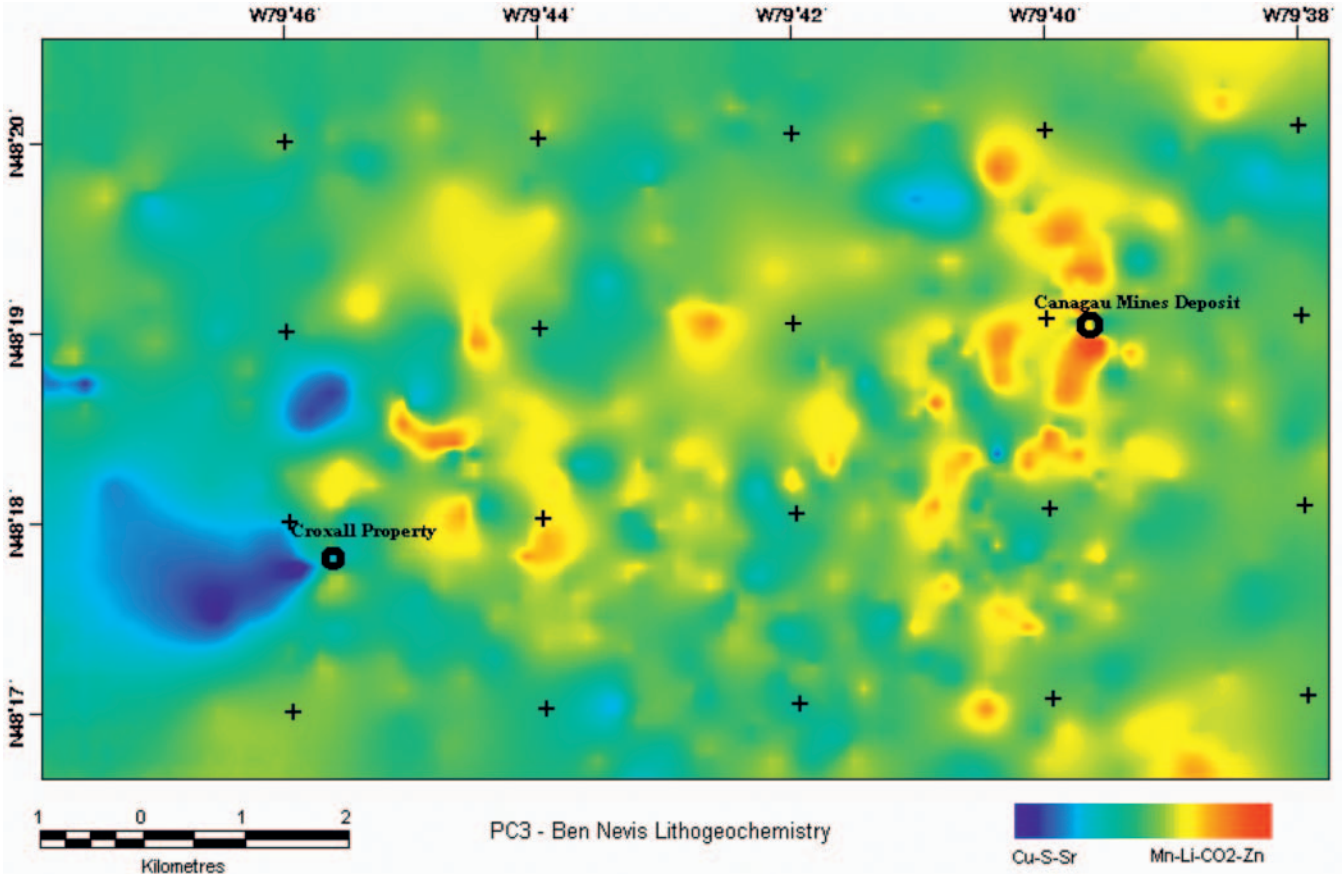


Plate 18. Image of the third principal component derived from the log-centred lithogeochemical data, Ben Nevis Township, Ontario. This image outlines the sulphide and mineralized occurrences.

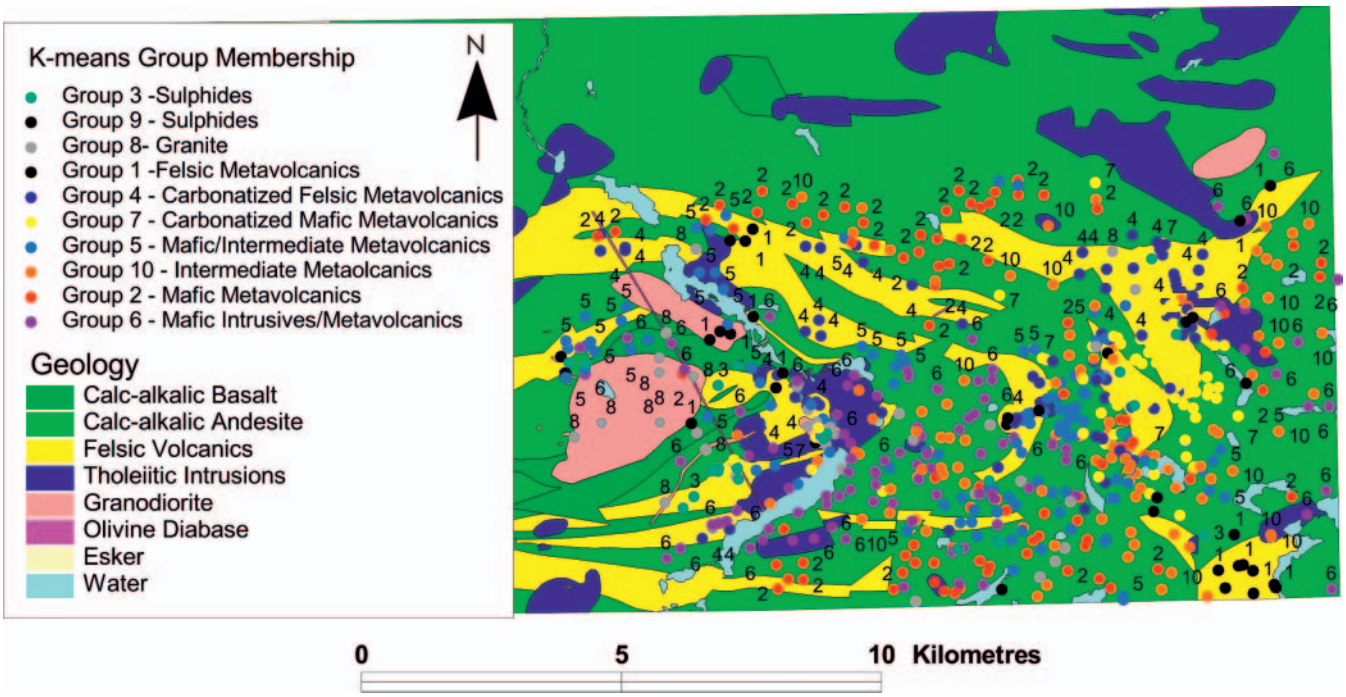


Plate 19. K-mean clustering of the log-centred lithogeochemical data, Ben Nevis Township, Ontario. Specific groups are associated with distinctive lithologies and zones of alteration and mineralization.

The biplot of Figure 17 shows a dominant trend associated with mineralization. This is due to the high density of sampling over mineralized terrain that is closely associated with sedimentary horizons within the volcanic assemblage of the area. The 'horse-shoe' effect in Figure 17 is due to the correlation between the two trends; highly mineralized samples are depleted in Na and K and

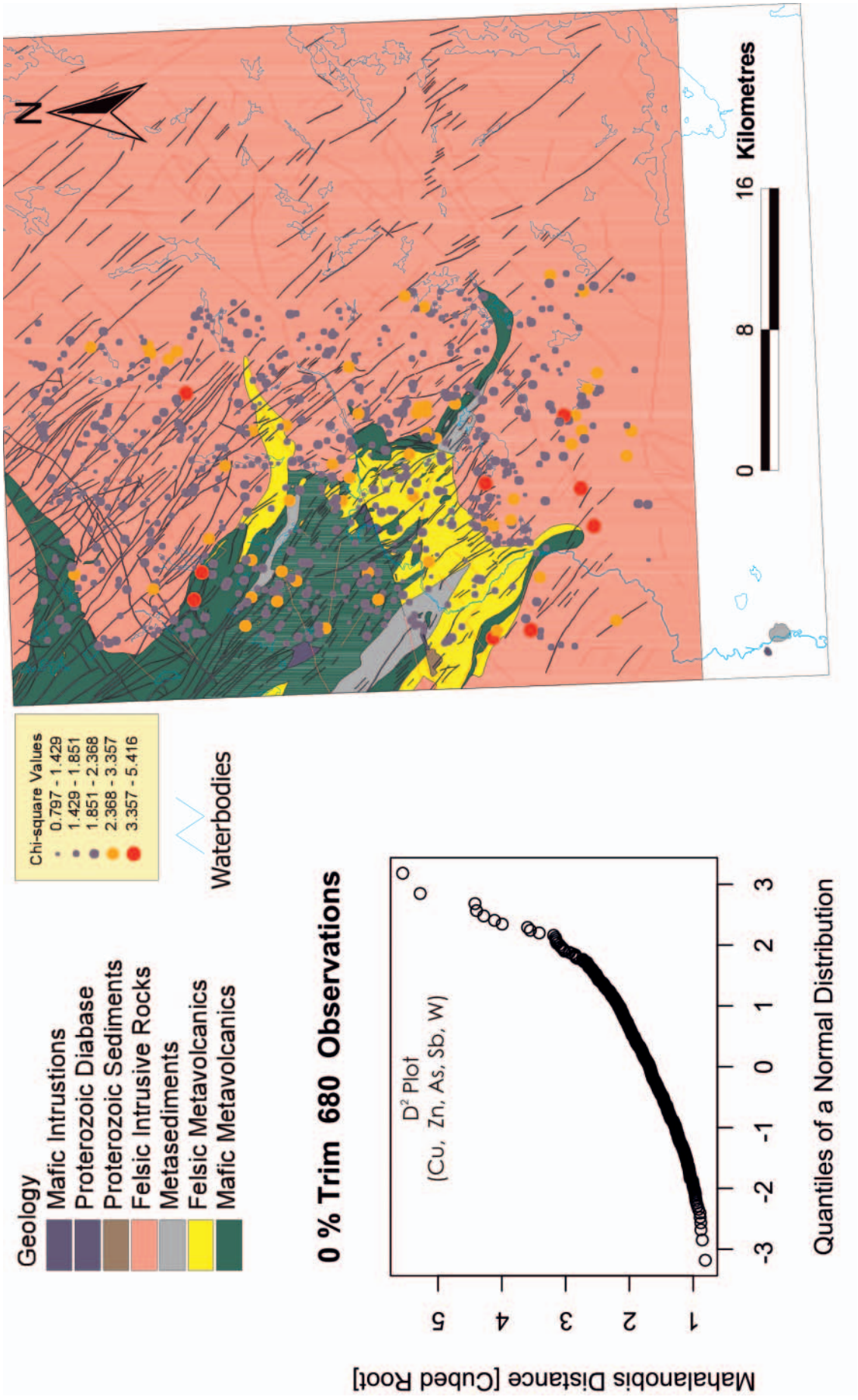


Plate 20. Plot of D^2 scores on the geological map. Sites highlighted in red indicate a significant departure from background and warrant further evaluation.

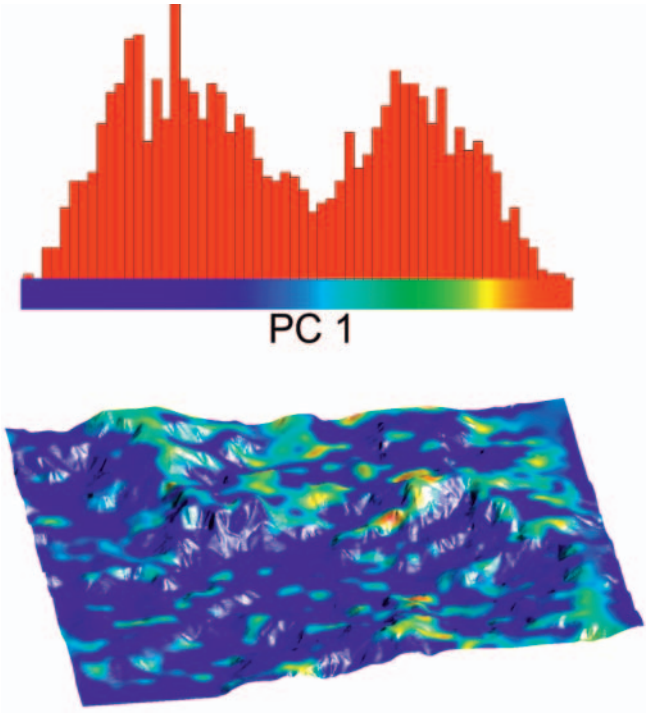


Plate 21. Interpolated scores of the first principal component draped over a digital elevation model for the area. Also shown is a histogram of the scores for the first principal component. The positive (right) side of the histogram is coloured and the corresponding colours are shown draped over the DEM. These areas are interpreted to be recent volcanic ash that have accumulated on hill tops and the windward-lee side of slopes.

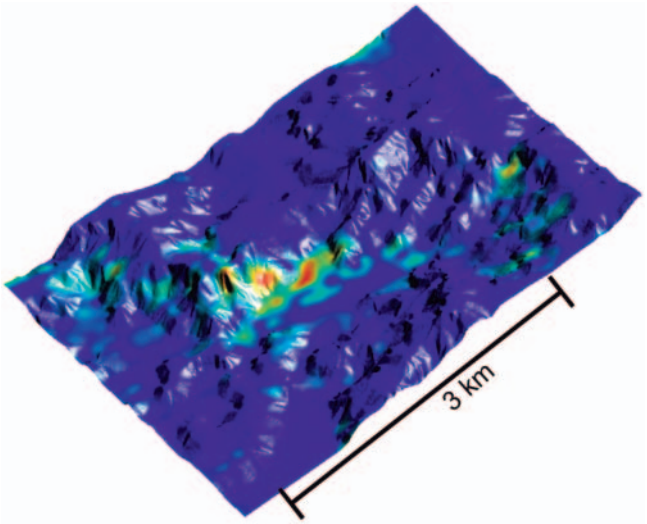


Plate 22. Interpolated scores of the second principal component draped over the digital elevation model. The image shows the Cu enrichment trend is mostly exposed along the valley walls in areas where the weathering is likely to be most active.

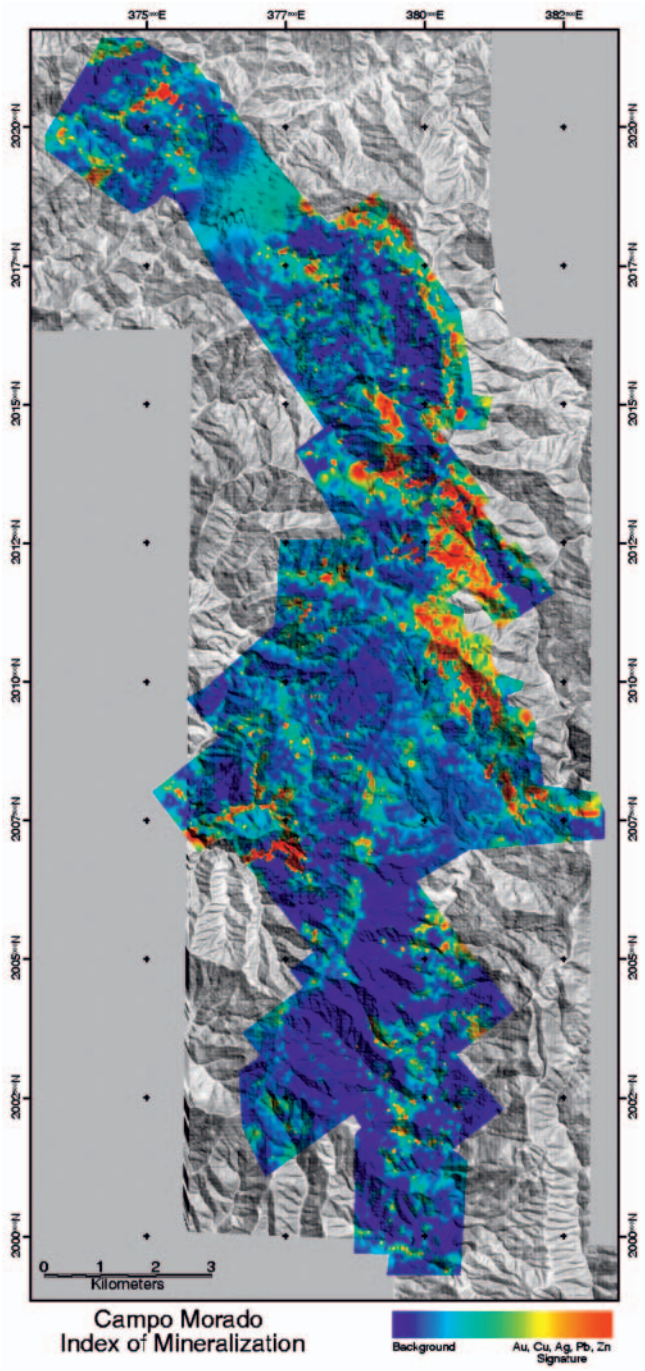


Plate 23. Plot of the interpolated PC1 scores over the digital terrain model in the Campo Morado area, Mexico. Areas highlighted in red are elevated in Au, Cu, Ag, Pb and Zn values. The image is termed as an 'index of mineralization'.

subsequently slightly more enriched (relatively) in elements associated with intermediate to mafic volcanic rocks.

A planimetric image of the second principal component over a shaded relief image of the DEM is given in Plate 23. Felsic volcanic rocks (red and yellow) are distinguished from mafic volcanic rocks (blue). Felsic rocks show relative enrichment in K and Na, while the mafic rocks show relative enrichment in Fe, Co, Ti, Mg, Cr, Al, Sc, and V. The areas highlighted in green represent lithologies of intermediate compositions and are mostly mudstones, argillites and sandstones. These are the host rocks for several of the mineral deposits in the Campo Morado area. The same image is shown in Plate 24 where it is draped over the DEM of the area. The first principal component highlights areas of relative enrichment of Ag, Zn, Au, As, Pb, Hg, Sb and Cu. These areas, shown in red and yellow, are potential sites of mineralization (Plate 23). This image is a three-dimensional rendering over the DEM. Examination of these areas in conjunction with the DEM assists in setting priorities for follow-up. Anomalies that lie along riverbeds or show significant dispersion must be treated with

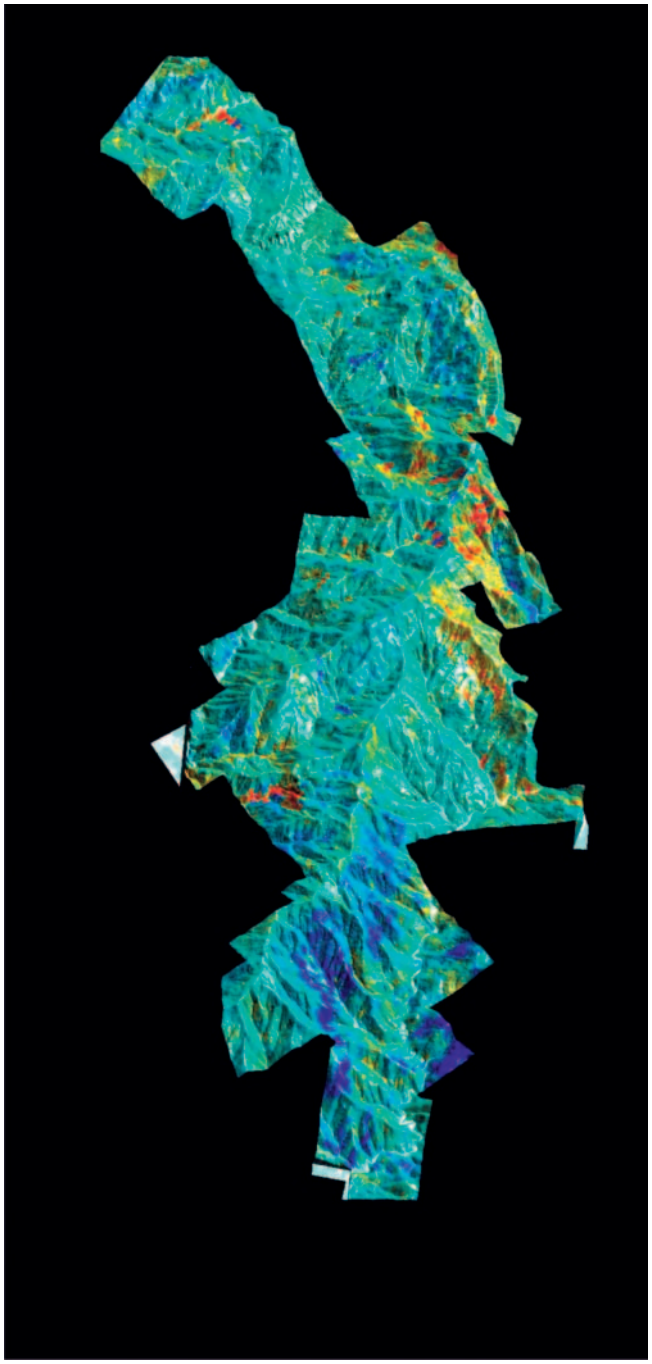


Plate 24. The index of mineralization is draped over the digital terrain model and rendered in 2.5D. This enhances the interpretation of mineralization with respect to the terrain variation.

caution due to the effects of hydromorphic and downslope creep dispersion effects.

CLASSIFYING GEOCHEMICAL DATA: AN EXAMPLE USING KIMBERLITE GEOCHEMISTRY

A suite of kimberlites has been evaluated, from an area in central Saskatchewan, Canada. A suite of 263 lithogeochemical samples selected from drill core was studied by Grunsky & Kjarsgaard (2008). This study followed an initial evaluation of the application of geochemical to characterize kimberlitic processes. (Kjarsgaard *et al.* 1997). On the basis of macroscopic core-logging observations, the data were partitioned into four

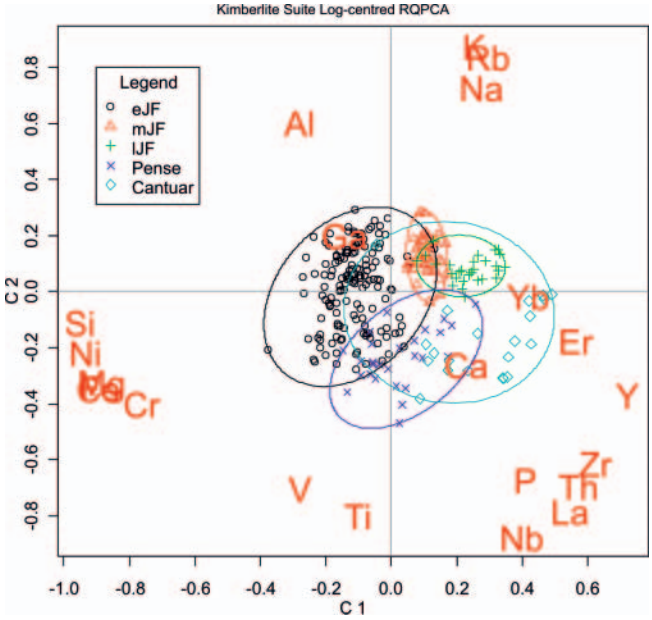


Plate 25. Biplot of the first two principal components derived from the kimberlite lithogeochemical data. Each kimberlite phase is shown by a different symbol and colour. The scores of the samples are shown as symbols. The corresponding scores of the elements are plotted as the element symbol.

distinct suites representing phases of the kimberlitic eruptions and contamination with surrounding country rock. The emphasis on this evaluation will be on the discrimination between the various eruptive phases and diamond-bearing versus non-diamond-bearing phases. In this example, the geographic coordinates have not been made available. As a result, a geospatial analysis has not been carried out.

The following major element oxides and trace elements were used in the evaluation: SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, Na_2O, K_2O, P_2O_5, Rb, Nb, Zr, Th, V, Cr, Co, Ni, La, Er, Yb, Y and Ga. Initially, the data were plotted as a large scatterplot matrix to examine the distributions and associations amongst all of the major element oxides and trace elements. Figure 18a and b shows a scatterplot matrix for Yb, P, La, and Zr. These four elements show a range of compositional variation that reflects kimberlite fractionation. Figure 18a shows distinct differences between the kimberlite phases with clearly defined linear relationships that reflect the stoichiometry of the individual mineral assemblages. Figure 18b shows the same elements after applying a logcentre transform. The overall distinctiveness of the individual kimberlite phases is readily apparent; however, the logcentre transform has distorted the linear stoichiometric relationships. Figure 18b provides the basis for calculating statistical measures of association through the application of a logcentred transform. Both figures are important and useful in understanding the nature of the multivariate geochemical relationships in kimberlitic rocks. Note that the phases of kimberlite show variable degrees of distinction. In both Figure 18a and 18b, the early- (eJF) and mid-Joli Fou (mJF) phases are less distinct than those of the late-Joli Fou (lJF), Cantuar and Pense phases. Note, also, that the phases do not appear to be homogeneous in their distribution, which can cause some difficulty in describing their differences within a statistical framework.

RQ-mode PCA was applied to the centred logratio data and the results are shown in Table 5. Nearly 90% of the data variation is accounted for by the first seven components. These components were subsequently used to find groups in the data

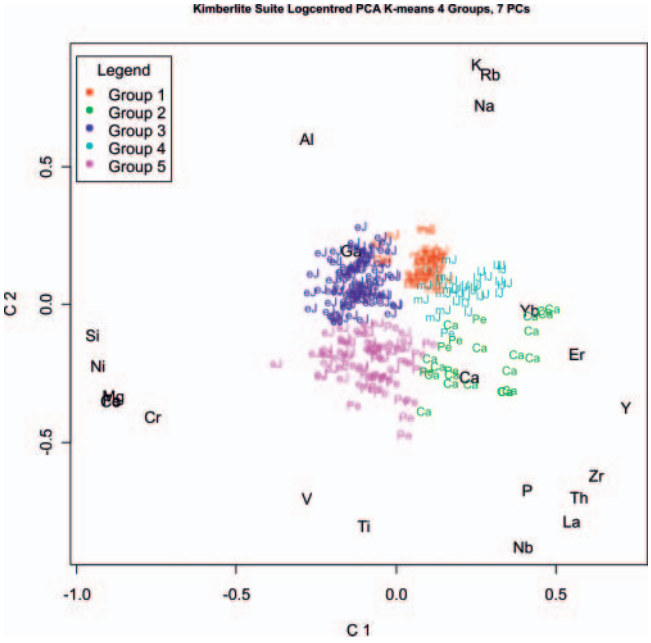


Plate 26. K-means clusters for five groups from the kimberlite data based on 7 principal components. The observations are labeled according to suite membership and coloured according to K-means group membership.

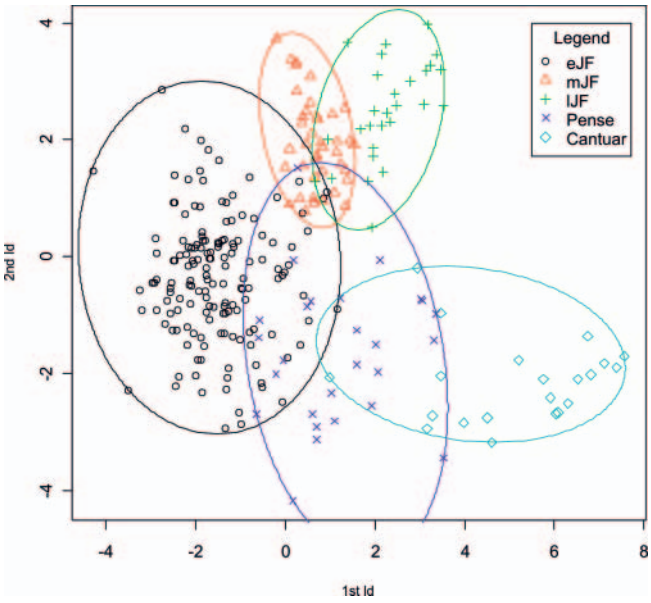


Plate 27. Linear discriminant plot of the first discriminant functions. Note the overlap between the kimberlite phases. See text for a more detailed explanation.

and apply linear discriminant analysis. Grunsky & Kjarsgaard (2008) provide further details on the evaluation and interpretation of the lithogeochemical data including the use of *k*-means cluster analysis as a means to confirm the distinctive groupings of the kimberlite phases.

Plate 25 shows a biplot of the first two principal components with the observations coloured to represent the four phases of the kimberlite data based on core-logging criteria. These two components represent more than 65% of the total variation and formed the basis of a subsequent cluster analysis. The overlap of the groups is shown clearly in this figure. For the most part, the groups are distinct, but the early-Joli Fou, Cantuar and Pense phases are inhomogeneous. As a result, there is likely to be some confusion when classifying unknown samples. However, the scenario, as presented here, is typical of geochemical classification problems.

Following the initial evaluation of the data using PCA, the data were subjected to a *k*-means cluster analysis using software from Venables & Ripley (2002). It was reasoned that, from the patterns exhibited in the first two principal components and from observations based on core-logging studies, the five phases of kimberlites could be discriminated using the group of 22 elements. The *k*-means cluster analysis for five groups was carried out on the first seven principal components and the results of the analysis are shown graphically in Plate 26. The choice of five groups was based on petrographical evidence combined with the observed clusters through several trial and error procedures of using *k*-means clustering. A choice of five groups split the data into groups that were coincident with the five major kimberlite phases. Plate 26 shows that the early-Joli Fou and Pense phases are clustered into Groups 3 and 5. On the other hand, the mid- and late-Joli Fou groups are sufficiently distinguished as separate groups (1 and 4). The Cantuar phase (Group 2) shows a small amount of overlap with the Pense phase.

Given the statistically distinct groups based on the k-means clustering, linear discriminant analysis was applied to the data using the phases of the kimberlite as classified based on core-logging observations. Linear discriminant analysis (lda) was applied to the seven principal components derived from the geochemical data using methodology described by Venables & Ripley (2002). For discriminant analysis, a centred logratio covariance results in a singular matrix because the inverse of the covariance is required. For this reason a logratio transformation was applied using Ga as the divisor. The results of the analysis are shown graphically in Plate 27. The plot reveals reasonably good discrimination between the suites of kimberlites. Although there is overlap between the groups, the overall discrimination is quite good.

Diamond content is directly related to specific suites in the kimberlites. Elevated diamond content is associated with those samples affiliated with more mafic material, most notably in the rocks of suite B. The posterior probabilities generated by the linear discriminant analysis show that the designated suites are clearly separable on the basis of lithogeochemistry.

Table 6 provides measures of the types of errors that occurred in the classification. The overall accuracy of 91.9% is the percentage ratio of the total number of correctly classified observations divided by the total number of observations for all eruptive phases. The terms used in the measures of accuracy are described in Appendix 3. The error of commission for each eruptive phase is the percentage of observations belonging to another eruptive phase, yet assigned the eruptive phase of interest. These errors are 5.3%, 6.7%, 16.0%, 17.9% and 9.5%, respectively, for the eJF, mJF, lJF, Pense and Cantuar eruptive phases. This is also reflected by examining the rows of the confusion matrix (Table 6) that show to which eruptive phases some of the observations have been assigned. The error of omission for each eruptive phase is the percentage of observations that belong to a given eruptive phase but have been assigned to another eruptive phase. These errors are 3.9%, 17.8%, 4.0%, 21.4% and 4.8%, respectively, for the eJF, mJF, lJF, Pense and Cantuar eruptive phases. The columns of the confusion matrix (Table 6) indicate to which eruptive phase the observations have been assigned.

The user accuracy of Table 6 is a measure of percentage ratio, for each eruptive phase, of correctly classified observations divided by the total number of observations that has been

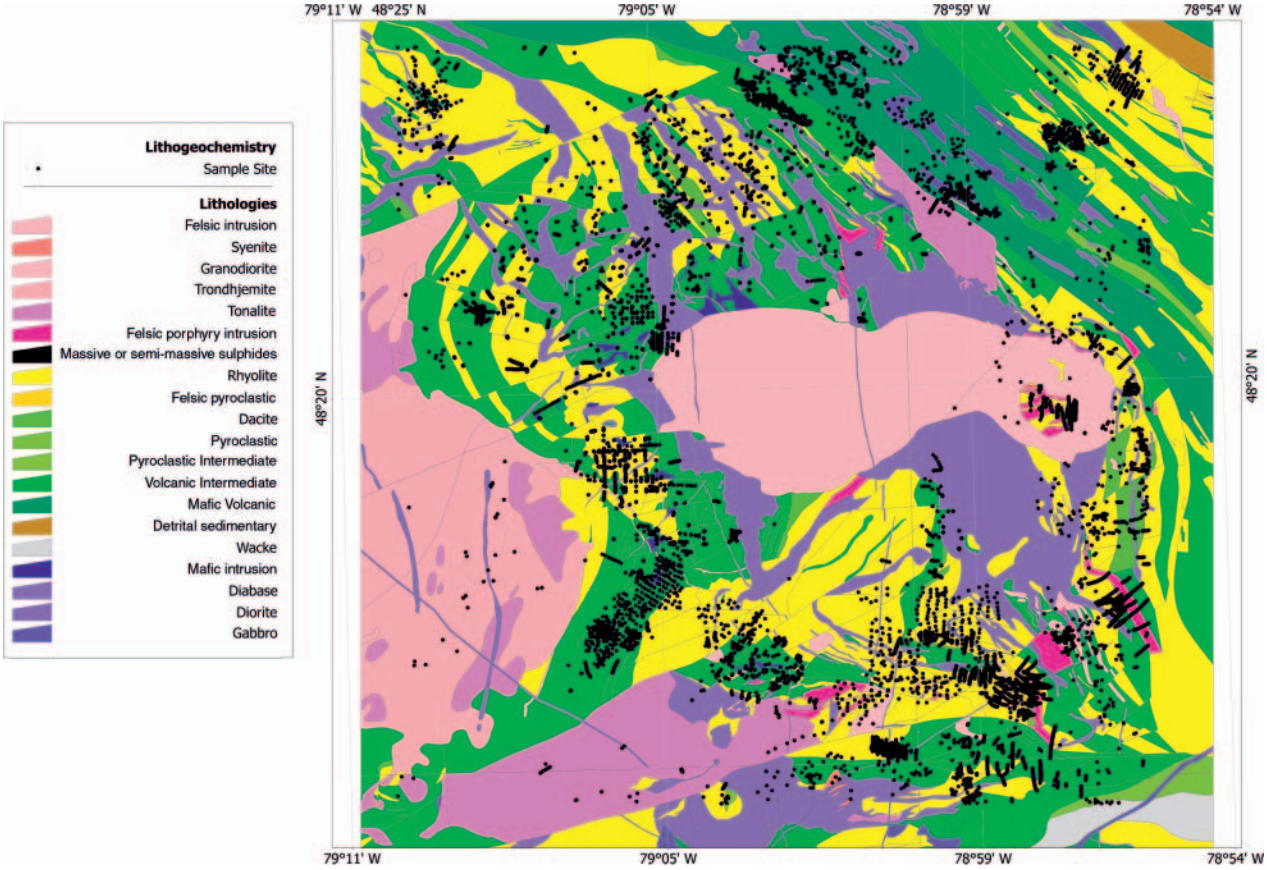


Plate 28. Planimetric map of lithologies and sample location points in the central Noranda area, Quebec.

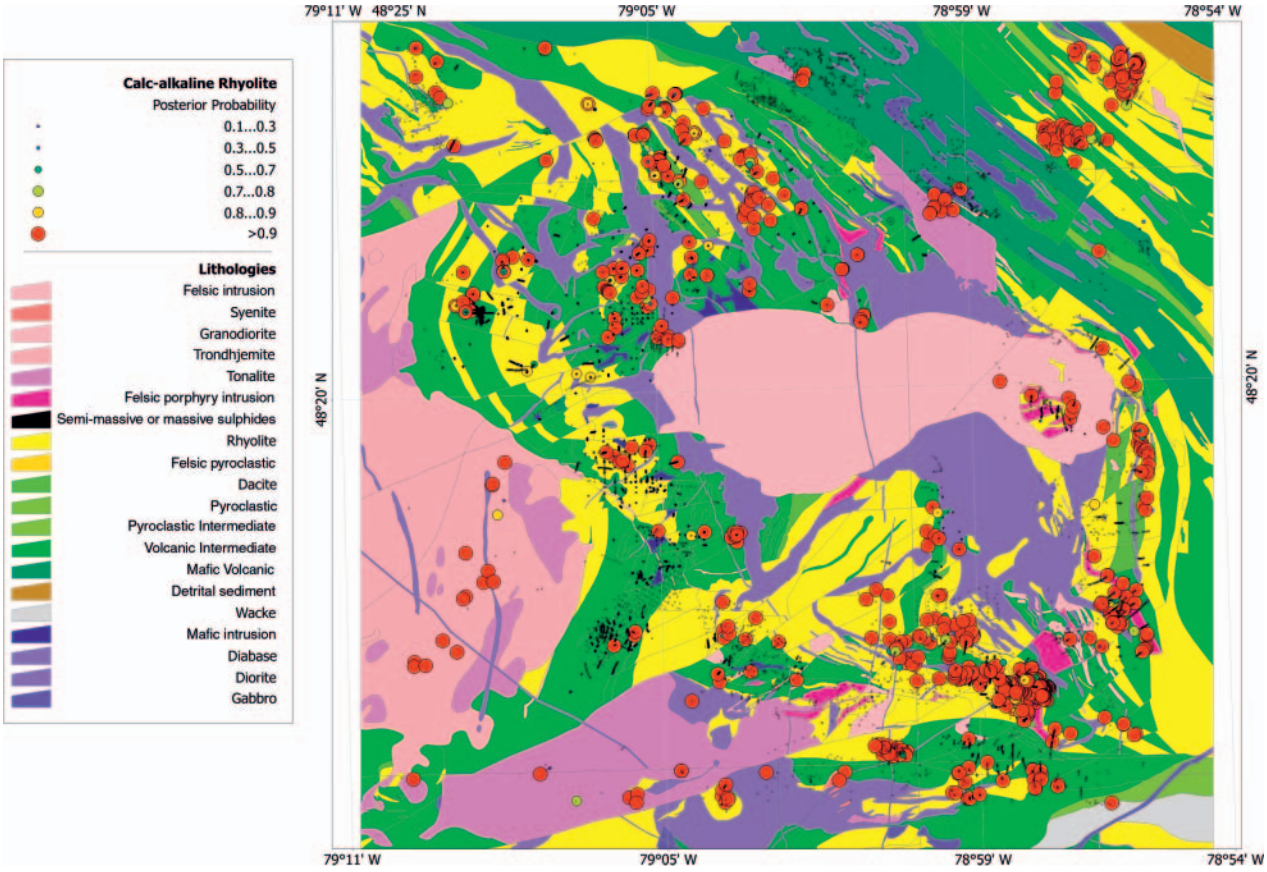


Plate 29. A map of posterior probability for a given sample being classed as a calc-alkaline rhyolite as described in the text.

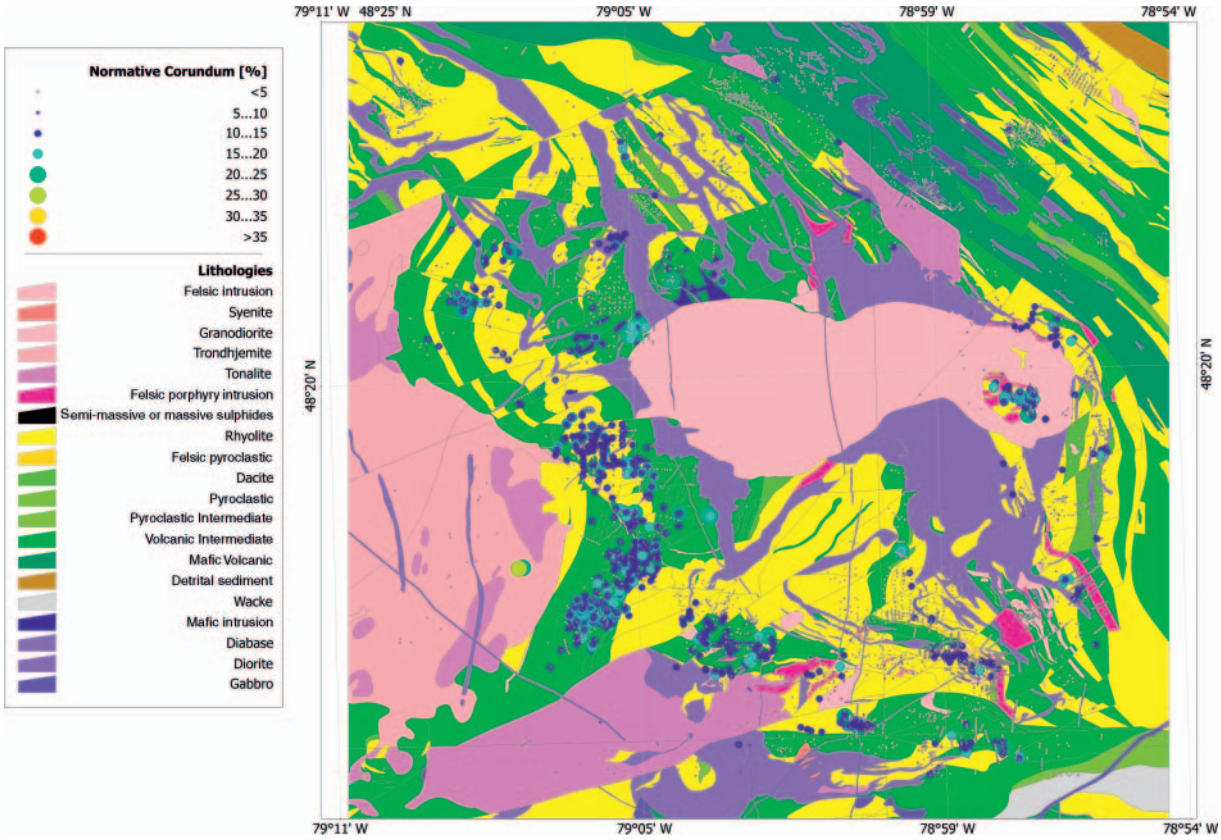


Plate 30. Normative corundum values plotted on the geological map of the central Noranda area. High normative corundum indicates a relative enrichment of Al over the alkali elements (Ca, Na, K) and is a likely indicator of alteration through alkali mobility.

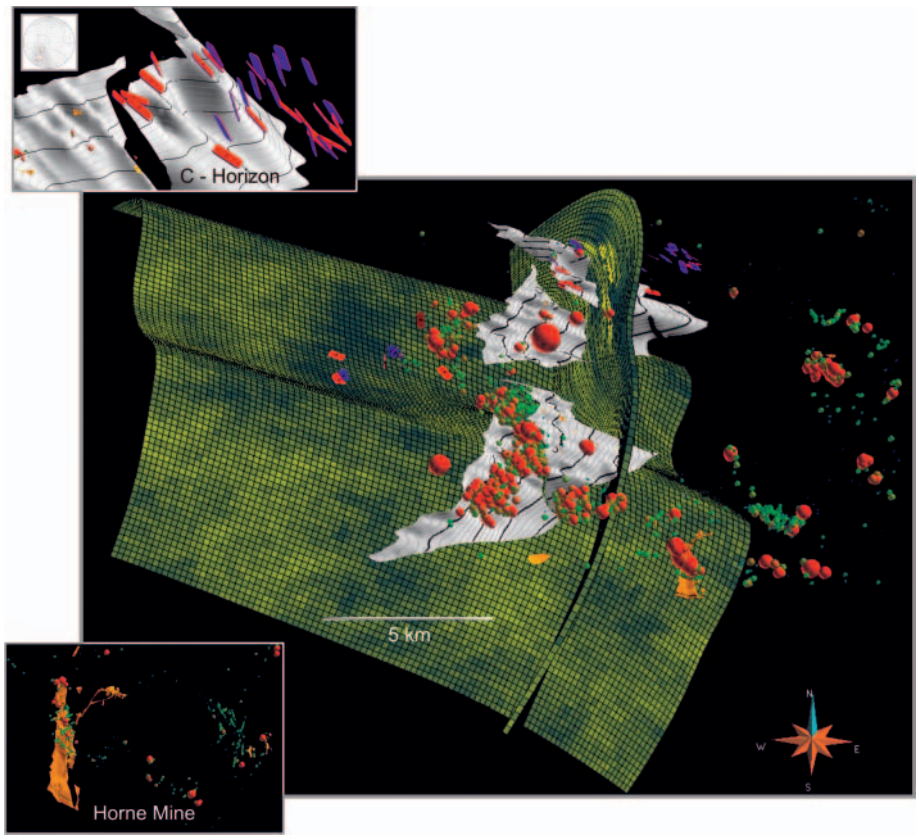


Plate 31. Three dimensional visualization of normative corundum using data spheres of normative corundum and volcanic isosurfaces derived from probability estimates of volcanic class designation.

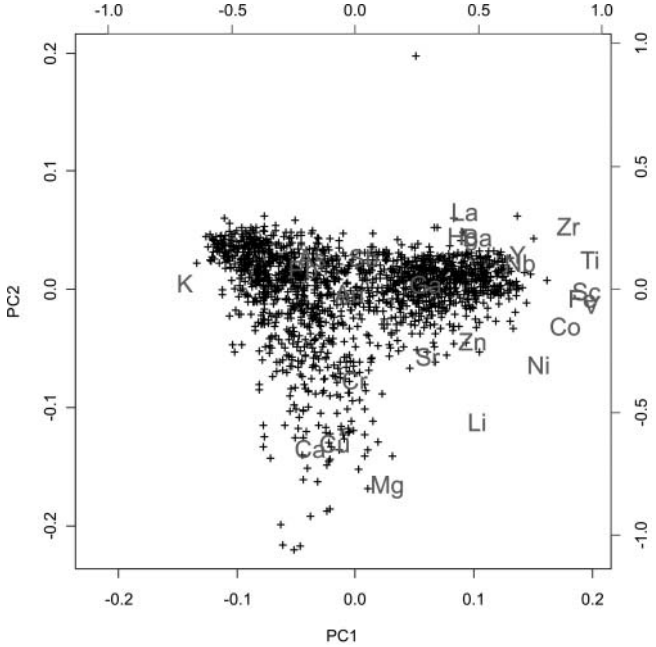


Fig. 16. Biplot of the first two principal components of the soil survey geochemical data from the island of Sumatra. Note the two distinct populations that represent the saprolite and volcanic ash.

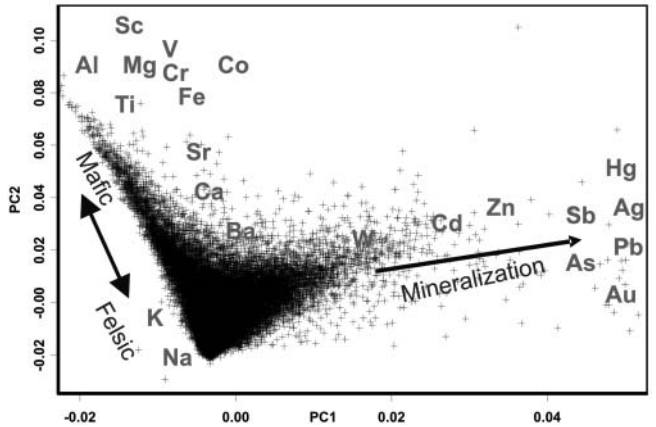


Fig. 17. Biplot of the first two principal components from the geochemistry of the Campo Morado soil survey data. Note the significant correlation of PC1 with PC2, which is the result of relative depletion of Na and K from the volcanic rocks and the mineralized areas.

assigned to each eruptive phase. The producer accuracy of Table 6 is a measure, for each eruptive phase, of the number of observations correctly classified divided by the number of observations that actually belong to the eruptive phase. Both measures of accuracy show high values for the eJF, mJF, and lJF phases and a lower accuracy for the Pense and Cantuar eruptive phases. This lower accuracy is a reflection of the higher degree of dispersion of the Pense and Cantuar observations and subsequent overlap with other eruptive phases.

The use of principal component analysis as a mechanism for classifying the data is based on the ability to recognize distinctive geochemical processes, as outlined previously. The application of the discriminant analysis applied to the first seven components confirms that these linear combinations of data describe variation associated with specific processes and that the classification accuracies are acceptable.

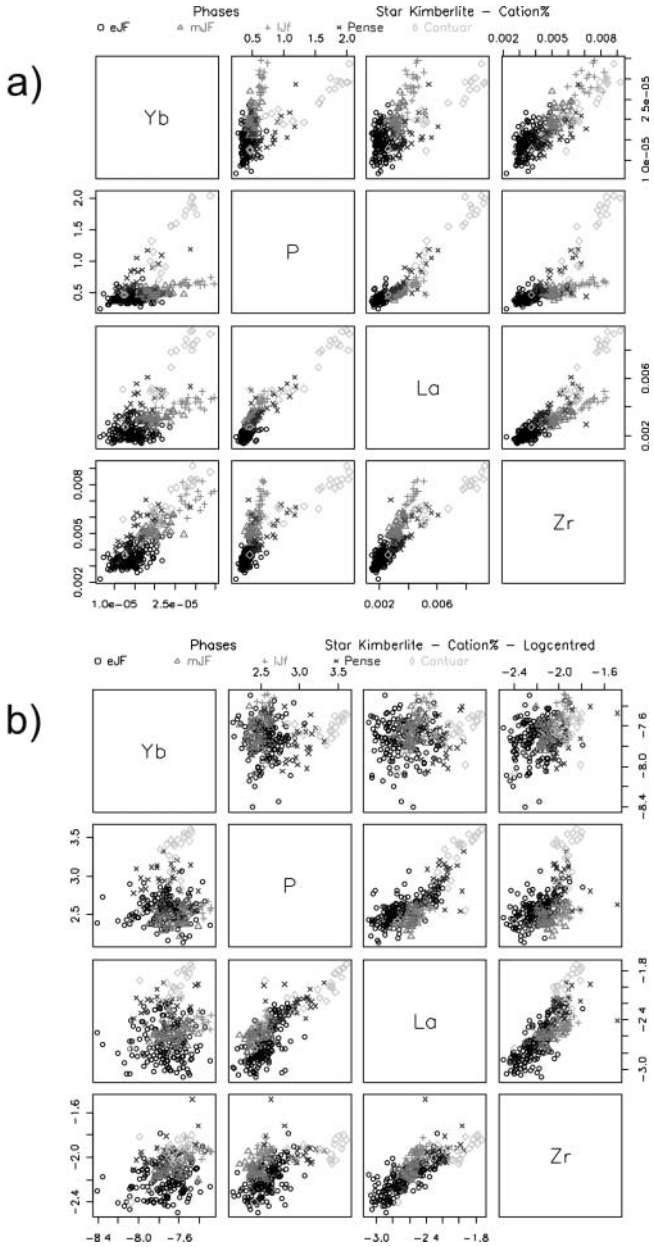


Fig. 18. Scatterplot matrix of elements associated with kimberlite magma fractionation. Plate 24a shows the distinctions between the kimberlite phases in different symbols and colours for the raw untransformed data. Plate 24b shows the same data after the application of a logcentre transform. See the text for a more detailed explanation.

APPLICATION OF LITHOGEOCHEMISTRY IN A 3D ENVIRONMENT, NORANDA CAMP, QUEBEC

Recent studies of a large lithogeochemical database from Ontario and Quebec, Canada, have highlighted the usefulness of using three-dimensional imaging from a set of diverse geological data for the purpose of geological modelling and mineral exploration projects. Data from various sources in Ontario have been assembled into an Open File Report (Hillary *et al.* 2008) that contains databases that can be used for subsequent evaluation by mineral exploration companies and detailed mapping in geological surveys.

A group of 17 164 lithogeochemical samples were processed using the R statistical package. These data were derived from

Table 5. *RQ-Mode principal components analysis of the 5 phase kimberlite data.*

Eigenvalues	PC1	PC2	PC3	PC4	PC5	PC6	PC7
λ	7.54	7	2.34	0.85	0.84	0.6	0.55
λ%	34.41	31.94	10.66	3.89	3.82	2.74	2.5
Σλ%	34.41	66.36	77.01	80.9	84.73	87.47	89.97

R-Scores	Values <0 in italics						
	PC1	PC2	PC3	PC4	PC5	PC6	PC7
Si	*−0.95*	*−0.11*	*−0.14*	*−0.09*	*−0.06*	0.04	*−0.08*
Ti	*−0.1*	*−0.8*	*−0.02*	0.16	*−0.31*	0	0.31
Al	*−0.28*	0.61	*−0.61*	0.13	0.07	*−0.03*	*−0.08*
Fe	*−0.89*	*−0.34*	0	*−0.14*	0	*−0.01*	*−0.1*
Mg	*−0.88*	*−0.33*	*−0.19*	*−0.09*	0.06	*−0.05*	*−0.11*
Ca	0.23	*−0.26*	0.54	0.35	0.57	0.32	*−0.01*
Na	0.27	0.73	0.09	0.08	*−0.37*	0.38	0.01
K	0.25	0.88	0.18	*−0.08*	0.06	*−0.28*	0.07
P	0.41	*−0.67*	0.25	*−0.2*	0.2	*−0.15*	*−0.24*
Rb	0.29	0.84	0.19	*−0.07*	0.03	*−0.32*	0.12
Nb	0.4	*−0.87*	0.09	0.08	*−0.15*	*−0.04*	*−0.02*
Zr	0.62	*−0.61*	*−0.24*	0.07	*−0.12*	*−0.05*	0.06
Th	0.57	*−0.69*	*−0.01*	0.03	*−0.2*	*−0.02*	*−0.19*
V	*−0.28*	*−0.7*	*−0.09*	0.16	0.24	*−0.22*	0.4
Cr	*−0.76*	*−0.4*	*−0.15*	0.12	*−0.04*	0.04	0.1
Co	*−0.89*	*−0.34*	0.07	*−0.13*	0.02	0.02	*−0.02*
Ni	*−0.93*	*−0.22*	0.07	*−0.16*	0.03	0.05	*−0.05*
La	0.55	*−0.78*	0.11	*−0.03*	*−0.08*	*−0.07*	*−0.1*
Er	0.56	*−0.17*	*−0.57*	*−0.18*	0.2	0.06	*−0.05*
Yb	0.42	*−0.01*	*−0.64*	*−0.37*	0.19	0.25	0.26
Y	0.72	*−0.37*	*−0.4*	*−0.12*	0.06	*−0.01*	*−0.07*
Ga	*−0.14*	0.2	*−0.69*	0.56	0.06	*−0.13*	*−0.2*

government surveys and mineral industry drill-hole data in both surface geographic coordinates and three-dimensional geographic coordinates. The data were compiled and organized as follows:

1. Use samples with the following minimum information: SiO_2, Al_2O_3, FeO, MgO, CaO, Na_2O, K_2O, P_2O_5, MnO, TiO_2 and LOI (loss on ignition).
2. Cation equivalent values were computed for each sample.
3. Normative minerals were computed using a standard Barth-Niggli normative classification scheme.
4. The samples were classed according to the two volcanic classification schemes of Irvine & Baragar (1971) and Jensen (1975).
5. The samples were logcentre transformed and then classified using a linear discriminant analysis based on reference groups defined by Grunsky *et al.* (1992).

Plate 28 shows a planimetric map of the samples projected to the surface. Drill-hole sample data are projected onto the surface resulting in a denser pattern of points that is not actually present on the surface.

Grunsky *et al.* (1992) developed a set of reference groups representing typical volcanic compositions using the classification of scheme of Jensen (1975). Each composition from the central Noranda area was classified using a linear discriminantanalysis as documented in Venebles & Ripley (2002). Posterior probabilities of rock type membership were derived for each sample from which maps can be created that depict the likelihood of rock type based solely on the lithogeochemistry. A logcentred transform was applied to the data and reference groups prior to the classification. For the classification, LOI was used as the divisor for the logratio transform. Plate 29 shows a map of the likelihood of a sample being classified as a rhyolite. The application of this type of scoring is that it provides a classification that is independent of the geological map and can help define lithologies in areas where the surface or subsurface geology is not known.

Many methods exist for assessing alteration of volcanic rocks. An initial measure of alkali alteration and migration can be demonstrated through the calculation of normative mineral procedures. The use of normative mineral procedures is well established (Yegorov *et al.* 1988; de Caritat *et al.* 1994; Cohen & Ward 1991; Merodio *et al.* 1992; Rosen *et al.* 2000; Piche & Jebrak 2004). When corundum occurs in the calculated norm (Plate 30), it generally signifies the mobility of Na, K and Ca, which can be associated with alteration signatures associated with base- and precious-metal mineralization.

Plate 31 shows normative corundum (diagnostic of alkali alteration) plotted in GoCad® by Eric de Kemp (Geological Survey of Canada, pers. comm.) indicating an association with known mineral deposits in the central Noranda camp area. The map is a down-plunge multi-parameter 3D model of northern Central Noranda mining camp, Quebec, Canada, combining ore bodies, regional geometry, structural observations, a lithological simulation and a geochemical classification. Volcanogenic Massive Sulphide (VMS) deposits are depicted as orange irregular surfaces with the Horne mine in the foreground (lower left inset). The deformed stratigraphic grid (in green) represents the mean of realizations for felsic volcanic lithologies with bright orange (90%) and blue (< 10%) probabilities. An exhalite stratigraphic unit (C-Horizon) is shown as a white surface (inset upper left) contoured at 1 km depth intervals with outcrop dip measurements depicted as blue-red tablets with a Wulff net plot of 42 structural observations. Variably sized spheres (green–red) represent normative corundum values > 5%. Geochemically, highly altered zones are represented by the largest red spheres. An east–west horizontal white cylindrical scale bar is shown at the ground elevation.

Table 6. *Measures of confusion, accuracy and error based on the PC.*

Overall Accuracy (%) 91.9						
Confusion (numbers)	eJF	mJF	lJF	Pense	Cantuar	Total
eJF	146	4	0	4	0	154
mJF	2	37	1	0	0	40
lJF	0	4	24	0	0	28
Pense	4	0	0	22	1	27
Cantuar	0	0	0	2	20	22
Total	152	45	25	28	21	

Confusion (%)	eJF	mJF	lJF	Pense	Cantuar	Total (%)
eJF	94.8	2.6	0.0	2.6	0.0	100.0
mJF	5.0	92.5	2.5	0.0	0.0	100.0
lJF	0.0	14.3	85.7	0.0	0.0	100.0
Pense	14.8	0.0	0.0	81.5	3.7	100.0
Cantuar	0.0	0.0	0.0	9.1	90.9	100.0
Total (%)	114.6	109.4	88.2	93.2	94.6	

Error/Accuracy	eJF	mJF	lJF	Pense	Cantuar
Errors of Commission (%)	5.3	6.7	16.0	17.9	9.5
Errors of Ommission (%)	3.9	17.8	4.0	21.4	4.8
User Accuracy (%)	96.1	82.2	96.0	78.6	95.2
Producer Accuracy (%)	94.8	92.5	85.7	81.5	90.9

A STRATEGY FOR GEOCHEMICAL DATA ANALYSIS

Every set of geochemical data and area requires a unique approach in the application of methods to analyse and assess the data. The evaluation of geochemical data is an iterative and adaptive process. The methods of data analysis and visualization in both the geochemical and geographic spaces change throughout the procedure of discovery of geological/geochemical processes. Below is a list of suggested ways to evaluate data that should be considered in any investigation. Of course, not all steps are necessary or appropriate, but should serve as a guideline for a thorough investigation of geochemical data.

Preliminary data analysis

- Know your data! There is no substitute for spending time by evaluating the data using a wide variety of procedures so that associations and structures in the data can be identified.
- Examine each element with histograms, box plots, Q–Q plots, scatter plot matrix and summary tables.
- Use bubble or symbol maps to show the range and spatial variability of the elements of interest.
- Interpolated images can be used where appropriate.
- Trim the distribution of each element of gross outliers.
- Investigate outliers for each element (analytical error or atypical value?).
- Adjust data for censored values if required.
- Consider the application of logratio transformations (logcentred, isometric logratio) so that compositional data can be evaluated without the effect of 'closure'. This is necessary if measures of association are required (correlation, covariance).
- Apply measures of association using standard, as well as, robust procedures. Examine the differences and scrutinize the outliers.
- Test the data to see if the identification of patterns and outliers is improved by the use of transformations. Apply Box-Cox power transformations using observations below the 95th–98th percentile to determine the optimal transformation. The choice of transform parameters can be chosen visually (Q–Q plots, box plots, histograms) or by semi-automatic means.
- Examine scatter plots and Q–Q plots for the presence of multiple populations.
- If assembling datasets from diverse sources, examine the requirement for levelling.

Exploratory multivariate data analysis

The following is a summary of exploratory multivariate techniques.

- Create a scatter plot matrix of the raw data and transformed (logcentred ratios, isometric logratios) data. Look for trends/associations.
- Use robust estimates to compute means and covariances to enhance the detection of outliers.
- Apply dimension-reducing techniques, such as PCA, to identify patterns and trends in the data. Other methods such as non-linear mapping, multi-dimensional scaling and self-organizing maps may help discover structure in the data.
- Use geographic maps of the component scores to assist in identifying spatially-based geochemical processes.
- Apply methods such as cluster analysis to isolate groups of observations with similar characteristics and atypical observations. Specific groups of interest can often be isolated using these methods. Maps of the locations of the groups can help to examine the spatial continuity of the groups.
- Use robust Mahalanobis distance plots (D^2) applied to transformed data to assist in isolating outliers based on a selected number of elements of interest. Maps of large distances (>95th percentile) can assist in identifying observations or groups of observations of interest.
- Calculate specifically tailored empirical indices in areas where multi-element associations are well understood. The indices are based on a linear combination of pathfinder elements with coefficients that are selected for each area and commodity being sought. Observations with high indices can be investigated for mineralization potential.

- Visualize the results! Use GIS for visualizing data analysis/statistical results. Use the visualization features in programs, such as R, for a better understanding of the data.

Modelled multivariate data analysis

- Where target and background groups have been established, use procedures such as linear discriminant analysis (and variants) for testing the ability to classify sample groups of interest and to determine which elements provide the best discriminating power.

CONCLUDING COMMENTS AND FUTURE DIRECTIONS

Garrett (1989*a*) stated that the power of computers and capability of software would continue to grow along with a corresponding decrease in price. Almost 20 years later, that prediction still holds. Computers are not only more powerful, but they are more portable, which permits the most sophisticated processing even in the most remote parts of the planet. Developments in software, in terms of the amount of data capacity, developments in three-dimensional visualization and statistical methods have made enormous contributions to the way that exploration geochemists can evaluate and integrate all types of geoscience data. The rapid expansion of the internet has allowed new statistical communities to grow, such as the R project (www.r-project.org) in which thousands of statisticians and users throughout the world develop and contribute to an open source statistical software environment. Recent developments in freely available software (Grunsky 2002*b*) will make it easier to integrate geochemical data with geospatial data. In the R community, new statistical developments can be available to users within weeks and to anyone who has internet access. There is no doubt that this type of cooperative approach to the sharing of knowledge will increase the ability of geoscientists to extract as much information from their data as possible.

Another factor that has contributed to significant advancements in evaluating regional geochemical data is the ubiquitous development of internet resources for geochemical data availability. In addition, internet resources have contributed significantly to information on how to evaluate geochemical data. The internet itself is one of the first places one starts to 'mine' for data.

Discussions on the application of transformations of geochemical data have traditionally been based on raw analytical values and the potential problems associated with closure have not been taken into account. Further research is required in this field. There is ongoing research at the University of Girona, Spain, where the issues of evaluating compositional data are being addressed. Emphasis is being placed on research and the development of tools for the user.

Surprisingly, the scientific literature on levelling geochemical data is sparse. Levelling is routinely carried out in geophysical and geochemical programmes; however, a formal review of procedures has not yet been published. A full review of levelling methods applied to geochemical survey data is due.

Integrating spatially referenced data together with multivariate observations is an area that is undergoing many interesting developments. The use of fractals has been shown to highlight different spatial patterns that are attached to multivariate patterns and trends (e.g. Cheng & Agterberg 1994). Similarly the integration of multivariate statistics with geostatistical analysis is developing and will lead to new methods for extracting spatially-dependent multivariate patterns and trends.

Current implementations of statistics with GIS are not fully integrated and spatial statistics that are employed by GIS or image analysis systems offer limited analytical and developmental capability. Increased integration of multivariate methods together with spatial analysis will provide a comprehensive approach to assessing all spatially reference multivariate data. Multivariate geostatistics, which incorporates both the spatial and inter-element relationships, has been studied by only a few. Grunsky & Agterberg (1988, 1992), Grunsky (1990) and Wackernagel & Butenuth (1989) discuss two approaches to multivariate geostatistics. Bailey & Krzanowski (2000), Christensen & Amemiya (2003) and Krzanowski & Bailey (2007) discuss approaches to 'spatial factor' methods. Such methods will permit the simultaneous evaluation of geochemical processes within the geochemical and geospatial domain. The long-term benefit of this will be to identify geochemical processes as a function of spatial scale (sampling density) and will permit further discrimination between geochemical background and mineralization.

There are many data analysis and statistical methods available to assess geochemical data. This manuscript has reviewed and demonstrated the application of some of the more popular methods. Geochemists are encouraged to investigate the developing world of data analysis and statistical methods through projects such as R (www.r-project.org).

The author wishes to acknowledge helpful discussions with colleagues at CSIRO, Australia, and the Geological Survey of Canada and in the mineral exploration industry. Most notably, this includes Frits Agterberg, Norm Campbell, Graeme Bonham-Carter, Bob Garrett, Bruce Kjarsgaard, Harri Kiiveri, Barry Smee, Ray Smith and Jeremy Wallace. An earlier vision of this manuscript has also benefited from reviews by Robert Jackson, David Lawie and Graham Closs. The author gratefully acknowledges the contribution of Eric de Kemp for providing the 3D imagery of the processed geochemical data from the Noranda area of Quebec. The author wishes to acknowledge thanks to the following for permission to use their data: Ontario Geological Survey and the Ontario Ministry of Natural Resources for the provision of the digital elevation data for the Ben Nevis area of Ontario; Farallon Mining Ltd and Mark Rebagliati of Hunter Dickinson Inc., Vancouver, are also gratefully acknowledged for their full cooperation and permission to present the results of the Campo Morado geochemical study. Shore Gold Inc. is also thanked for permission to present the results of the kimberlite geochemical data from the Fort à la Corne area, Saskatchewan. This is Geological Survey of Canada contribution number: 20090302.

APPENDIX 1

Logratios and compositional data

Compositional data should be adjusted by the use of logratios. A compositional vector x defined by D component variables (elements). By definition, this vector will sum to a constant (100%) and as a result, the composition can be described by $D-1$ of the variables. A composition x can be transformed by

$$y_i = \log(x_i/x_D) \; (i = 1, \ldots, D-1)$$

There is no loss of information by choosing one of the variables as a divisor. This transformation is known as the 'additive logratio' (alr). The resulting logratio coordinates cannot be projected onto orthogonal axes because the axes are at 60° (Pawlowsky-Glahn & Egozcue 2006) and create difficulties when comparing compositions using different denominators. In particular, measures of distances between alr-transformed observations are not equal when using different denominators and the angles between vectors cannot be computed using a standard Euclidean inner product.

An alternative way of transforming a compositional vector is by applying the logcentered ratio, namely:

$$z_i = \log(x_i/g(x_D)) \ (i = 1, \ldots, D),$$

where $g(x_D)$ is the geometric mean of the composition. The logcentered ratio (clr) is useful because it preserves all of the variables in the composition. However, the inverse of the covariance matrix for this transform is singular, which requires a special generalized inverse procedure for computation.

An important aspect of assessing compositions is the calculation of an adequate measure of variability. This is done by the creation of a variation matrix, T defined by:

$$\tau_{ij} = \mathrm{var}\{\log(x_i/x_j)\} \ (i = 1, \ldots, d; j = i+1, \ldots, D)$$

and the mean, E, is expressed as:

$$\xi_{ij} = E\{\log(x_i/x_j)\} \ (i = 1, \ldots, d; j = i+1, \ldots, D)$$

The variability matrix T summarizes the contribution that any pair of variables makes in a sub-compositional analysis. For example, consider a major element oxide composition consisting of SiO_2, Al_2O_3, MgO, FeO, CaO, Na_2O, K_2O, TiO_2 and MnO. A sub-composition may be interested in examining the relationships of MgO, FeO and Na_2O. The amount of compositional variability that these elements will account for can be expressed by the sum of ($\tau_{MgO,FeO}$, $\tau_{MgO,Na2O}$, $\tau_{FeO,Na2O}$). This is an important concept in understanding the significance of sub-compositional data which will never fully explain the overall variation of the data.

More recent developments by Egozcue *et al.* (2003) have identified the isometric logratio (ilr), which is a transformation that defines compositional vectors in an orthonormal basis. A very simple explanation of this transformation is described in Pawlowsky-Glahn & Egozcue (2006). The application of the ilr transform requires the construction of 'balances', which are ratios of selected variables into groups (i.e. elements associated with a fractionation process versus elements associated with alteration). These balances are used to construct new variables that exist in an orthonormal base from which standard Euclidean measures can be calculated (mean, variance, etc.).

APPENDIX 2

The method of RQ-mode principal component analysis

Given a data matrix of m variables and n observations, a data matrix X can be scaled (i.e. correlation or covariance) to produce a $m \times n$ matrix W where

$W = V\Lambda^{1/2}U'$ where Λ = diagonal matrix of eigvenalues

V = eigenvector matrix of n × m WW′
U = eigenvector matrix of m × m W′W

By use of the Eckhart-Young theorem (Reyment & Jöreskog 1993), W can be re-written as

$W = F^R A^R$(R-mode solution) where $F^R = V$ and $A^R = \Lambda^{1/2}U'$

or

$W = A^Q F^Q$(Q-mode solution) where $A^Q = V\Lambda^{1/2}$ and $F^Q = U'$

F^R and F^Q represent the factor loadings for both the R and Q mode solutions, and A^R and A^Q represent the coordinates of the variables and objects (the scores) in the same factor space and can be plotted on the same figures. W is scaled to permit the projection of both F^R and F^Q in the same coordinate space. W can be standardized by:

$$W_{ij} = (1/n^{1/2})(x_{ij} - \bar{x_j}) \text{ where } \bar{x_j} = 1/n\sum x_{ij} \ (\mathrm{i} = 1, \mathrm{n})$$

which yields a variance covariance matrix from the minor product matrix W′W. W can also be standardized by:

$$W_{ij} = (s_j n^{1/2})^{-1}(x_{ij} - \bar{x_j}) \text{ where } Sj = \left[(1/n)\sum (x_{ij} - \bar{x_j})^2\right]^{1/2} \ (i = 1, n)$$

which results in a correlation matrix from the minor product matrix W′W.

The advantage of plotting both the scores of the variables and objects on the same diagram is that the relationships between the two can be more clearly observed. Samples with relative abundance of one variable over another will plot near the location of the score for that variable. Grunsky (2001) has written program code for this method of PCA for both the S-Plus and R computing environments.

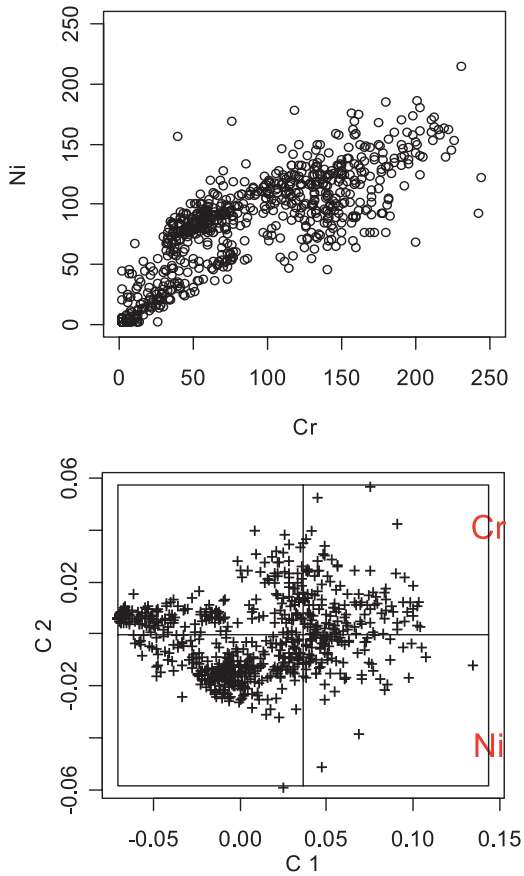
The relative contribution is the contribution that a variable makes over all of the components. It is defined as follows. For m variables (i=1,. . .,m), p components (j=1,. . .,p), ($p \leq m$) and the R-mode loadings given by A^R, the relative contribution rc_{ij} for a variable j is:

$$rc_{ij} = 100 * (A^R{}_{ij}/\sum_{j=1}^{p} A^R{}_{ij})$$

The actual contribution is the contribution that a variable makes within a given component. Similarly, the actual contribution is defined as follows. For m variables, p components ($p \leq m$) and the R-mode loadings given by A^R, the actual contribution $ac_{\tilde{n}}$ for a variable j is:

$$ac_{ij} = 100 * (A^R{}_{ij}/\sum_{i=1}^{m} A^R{}_{ij})$$

The following simple example illustrates the method of PCA.



RQ PCA Example.

The lithogeochemical data from the Ben Nevis township area in Ontario represents a suite of metavolcanics comprised of calc-alkalic basalt, anadesite, dacite and rhyolite. The sequence has also been intruded by tholeiitic mafic sills and granodiorite stocks. A plot of Cr v. Ni clearly shows the three main groups of the data.

The figure on the previous page top shows the linear relationship of Cr and Ni that is related to the mineralogy of the volcanic rocks. Rocks rich in minerals containing Cr–Ni (i.e. pyroxenes) are enriched in Cr and Ni whereas rocks that are poor in Cr–Ni bearing minerals (i.e. rhyolites, granites) are depleted in Cr and Ni. The results of the principal components reflect this same relationship. The three groups of data are still evident in the scatter plot of PC1 v. PC2. The loadings of Cr and Ni reveal the following information. Observations that plot on the positive side of the PC1 axis closer to the loadings of Cr and Ni are enriched in those elements and observations that plot on the negative side of the PC1 axis are depleted in Cr and Ni. In addition, observations that plot on the positive side of the PC2 axis are relatively enriched in Cr whilst those observations that plot on the negative side of the PC2 axis are relatively enriched in Ni and relatively depleted in Cr. Using the method of PCA, patterns in the resulting plots can assist in producing meaningful interpretations of the data.

PCA also reveals information about significance of each component. The first component (PC1) accounts for more than 92% of the variation in the data and the second component (PC2) accounts for *c.* 8% of the variation. Thus the first component is interpreted as the most significant and reflects the dominant geochemical process. The second component reflects a subtle feature that might be related to Cr–Ni variation in the more mafic observations.

APPENDIX 3

Measures of accuracy

- Confusion matrix: a cross-referenced matrix of classified samples for each class. Ideally, there should be zeros in every element of the matrix except along the diagonal. Each column represents a training class and the values in the column correspond to the classification results applied to that particular training class. The values can be expressed in the actual number of samples, or as a percentage.
- Commission: Errors of commission represent samples that have been incorrectly classified as belonging to the class of interest.
- Omission: Errors of omission represent samples that belong to a class of interest but have been classified incorrectly.
- Producer accuracy:a measure of correctly classified samples divided by the total number of samples used in the classification for a specific class of interest.
- User accuracy: a measure of correctly classified samples divided by the total number of samples classified to the specific class of interest.

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