



## THE CRITICAL IMPORTANCE OF MONITORING CHEMICAL ANALYSES IN FRONTIER EXPLORATION

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### ABSTRACT

*Mineral exploration activity has expanded in frontier regions in the last ten years where there is limited infrastructure. Local production-oriented laboratories have been established which are operating under difficult circumstances. Case histories are presented where poor data quality, including mislabelling of samples, sample cross-contamination and non-reproducible results, are documented from laboratories in frontier exploration regions. Rigorous quality control programmes are recommended to limit the risk associated with operating under these challenging conditions.*

### INTRODUCTION

The objective of this paper is to review the challenges encountered by laboratories in frontier regions of the world and recommend procedures to improve the quality of analytical data. There has been an extraordinary expansion of mineral exploration outside traditional areas of activity in the last decade. Mineral exploration companies continue to expand into new regions as governments alter tax and mining laws to attract foreign investment, and exploration programmes continue to be successful in locating mineral resources. The mineral explorationist is confronted with many challenges when operating in areas where infrastructure is underdeveloped and especially where there has been no recent private mine development. One service that is required, and often lacking, is a reliable analytical laboratory.

The commercial laboratories of Europe, North America and Australia have rapidly expanded to service the needs of exploration companies by investing in an estimated 25 new laboratories, primarily in South America, Africa and southeast Asia. An additional estimated 50 new commercial sample preparation facilities have been built as an additional convenience for exploration and mining companies operating in these regions. Although every effort is made to maintain analytical data quality, there are risks associated with using laboratories in a frontier situation due to challenges when operating under less than optimum conditions.

### OPERATING CHALLENGES FOR LABORATORIES

In general, it is preferable to use a local facility rather than add the cost of shipping samples to an overseas laboratory and encountering delays in shipping. Although it is rare, it is also possible for samples to be irretrievably lost. As reported in the Northern Miner Press of September 9,

1996, the IAMGOLD project in Niger experienced this problem when "The Saoura program was delayed when a plane carrying samples from the property crashed."

There are numerous challenges inherent in every production laboratory setting and special circumstances in frontier situations. Most problems can be assigned to two broad categories: lack of locally available services and consumables, and lack of communication between explorationists and laboratory staff. Some examples of the difficulties encountered in operating in remote locations are specified in Table 1. The effect of operating under these conditions and the impact on data quality and turnaround times are tabulated against the various operating constraints. The impact of operating under difficult conditions includes the possibility of accepting poor analytical precision and accuracy, sample cross-contamination, the application of inappropriate analytical procedures and long delays.

Poor data quality supplied by North American laboratories operating in more favourable conditions has been documented (Bloom, 1993; Fletcher, 1987; Hall *et al.*, 1989; Kretz, 1985; Levinson *et al.*, 1987) but the probability that these problems exist increases when operating under difficult conditions. The errors are not necessarily due to the negligence of laboratory staff or owners but are attributed to the operating conditions of the local situation.

### MONITORING CHEMICAL ANALYSES

Most laboratories implement a quality control programme based on routine duplicate analysis of pulps and analysis of reference materials (Fletcher, 1981). Blind quality control programs, recommended by geochemists for over 30 years, include the addition of hidden duplicates, control samples, third-party check analyses and randomization of samples

(Garrett, 1969; Hill, 1974; Howarth and Thompson, 1976; Plant, 1973; Plant *et al.*, 1975; Thompson, 1983). The use of certified reference materials is reviewed in Kane (1992), and compendiums of recommended values are included in Potts *et al.* (1992) and Govindaraju (1994).

Based on a survey of 50 international representatives at a 1996 geochemical workshop and personal experience, less than 1% of mineral exploration companies have a policy related to routine inclusion of control samples to commercial laboratories. Few examples of potentially embarrassing or litigious mistakes are published but most explorationists have personal experience with unsatisfactory laboratory results

A case history is presented here to demonstrate the effectiveness of a quality control programme for a frontier drill program. Data from a rigorous control programme, implemented by a mining company, has been generously contributed on an anonymous basis. Two fine-grained, homogeneous control samples were inserted routinely with sample pulps submitted to the laboratory. The results for Cu, Zn and Mo are plotted against batch number in control charts in Figure 1. The average Cu value for ControlA is 4235 ppm and individual results fall within  $\pm 2$  standard deviations of the mean with the exception of three values. The standard deviation of the data is 275 ppm (Figure 1a).

**Table 1: Challenges in operating laboratories in frontier conditions.**

Conditions	Effect	Impact
Power fluctuations	Calibration drift	Poor precision
	Computer failure Instrumentation failure	Reporting delays
Power failures	Instrument failure Lack of telecommunications	Reporting delays
Lack of locally available consumables	Fire assay crucibles imported at high cost or handmade resulting in a tendency to be re-used	Sample cross-contamination
	High cost to import quality fire assay litharge and possibly contaminated local litharge substituted	Poor accuracy and sample contamination
	Delays of imported goods in customs for 4-6 months are expected	Adversely affects turnaround time if insufficient materials are warehoused
	Hydrochloric acid, used in the production of cocaine, sometimes rigorously controlled	Higher costs and reporting delays
	Due to difficulties in acquiring fire assay consumables, other alternatives (aqua regia, BLEGS) considered	Poor precision Less than 100% gold extraction
Lack of trained local personnel	Analytical grade argon not available	Cannot operate ICP
	Language and cultural barrier with expatriate management	Incorrect or inappropriate procedures used Reporting delays
	Chief fire assayers require a minimum of five years experience and it is difficult to staff the position	Poor quality fire assays
	High rate of absenteeism due to diseases such as malaria	Inconsistent application of standard operating procedures
Inappropriate facilities	Local staff not familiar with currently available technology	Inefficiency and higher costs
	Adjoining preparation and laboratory facilities	Possible dust contamination
	High levels of humidity in tropical climates effects electronics unless air conditioning is maintained	Poor precision
General	Condensation of AAS fumes may contain up to 5 ppm Au and condensate may drip into sample solutions	Sample contamination
	No local instrument service technicians resulting in high travel costs and delays when instrumentation is inoperable	Reporting delays
	Unreliable telecommunications	Reporting delays

The plot of Zn values for the same control sample (Figure 1b) clearly identifies a significant problem. Five of the reported values for Control A are significantly higher than the general trend of the values. Excluding these five values, the average Zn value is 60 ppm and the standard deviation of the population is 16 ppm. The five values which lie outside the mean-plus-two standard deviation envelope (Zn equal to 92 ppm), range from 250 to 1100 ppm Zn.

A common cause of extreme variations in control samples is sample mix-ups. Both Cu and Zn were determined on the same solution, therefore Cu values for the control samples with erroneous Zn values were examined. The Cu values fall within the accepted range of variation and therefore do not support the supposition that the control samples were misplaced in the batch.

The cause of the erroneous Zn values has been attributed to incomplete washing of the sample probe used to introduce the digest solution to the atomic absorption spectrophotometer (AAS). Automated sampling

devices are designed to aspirate a solution, return to a distilled water wash beaker for cleaning and then aspirate the next solution in the test tube rack. In general, the washing step sufficiently cleans the solution from the sampling probe and capillary uptake tube prior to being inserted into the next sample solution. However, samples in these batches included drill core with grades in excess of 20% Zn, and the carry-over from the high grade samples is sufficient to influence the results of subsequent samples.

There are two possible methods to correct solution carry-over. The laboratory can be requested to increase the washing time between solutions. This will reduce the sample throughput and decrease productivity. Alternatively, when highly mineralized samples are recognized by a geologist, these materials could be submitted separately from other samples to reduce the probability of sample cross-contamination in preparation and analysis.

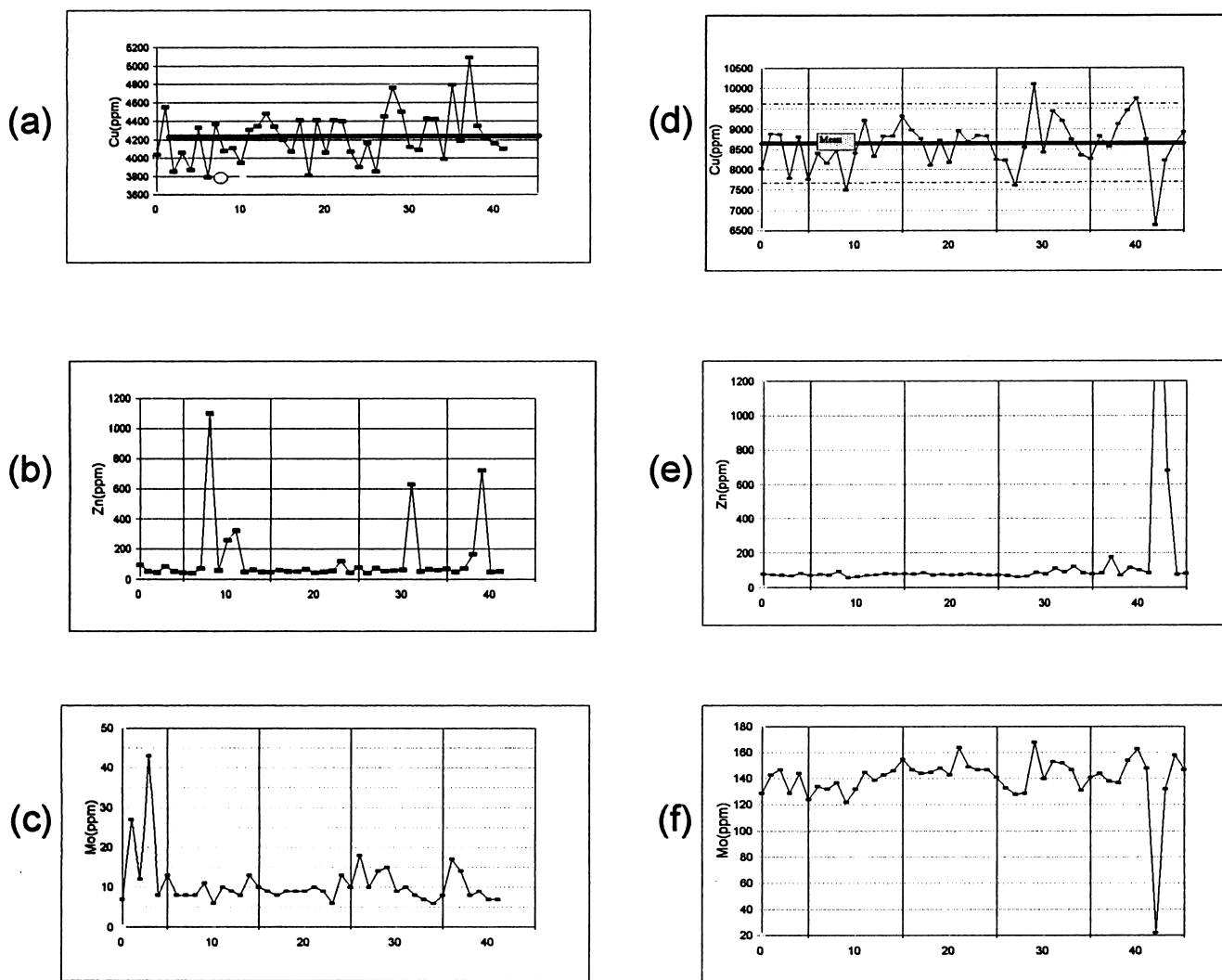
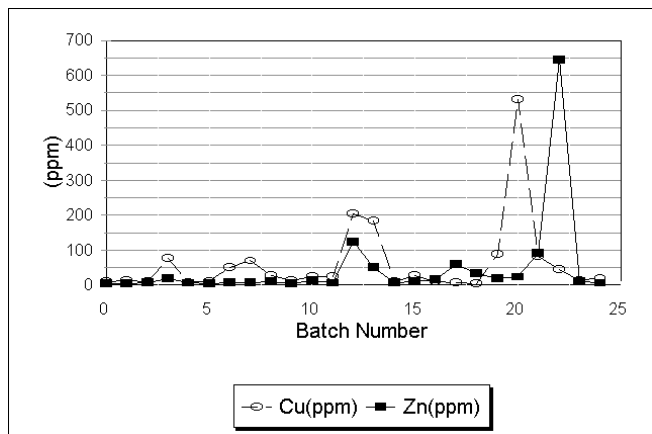


Figure 1: (a) Cu, (b) Zn and (c) Mo for Control Sample A plotted in sequence as submitted for analysis; (d) Cu, (e) Zn and (f) Mo for Control Sample B plotted in sequence as submitted for analysis.



**Figure 2:** Cu and Zn values for a barren sand sample plotted in sequence as submitted for analysis.

The results for Control B do not demonstrate the same effect, presumably because the control sample was not introduced immediately following a highly mineralized sample. However, the control charts for Control B (Figure 1d to 1f) identify a different type of problem. The 43rd insertion of Control B has anomalously low Cu and Mo results and an anomalously high Zn result.

Molybdenum was determined on a different digest solution than Cu and Zn. It is unlikely that the control sample was weighed incorrectly when the sample was prepared for both digestion procedures. The control sample was most likely mislabelled when inserted in the batch during sample preparation. Any of the drill core samples before or after the insertion of the control sample may also be mislabelled unless there are other control samples in the batch that are located properly. It is not possible to resample the drill core, but the crushed reject material must be pulverized again and reanalysed for a selection of samples, presumably at the expense of the laboratory. These pulps should be resubmitted with other control samples inserted in the batch.

Efforts have also been made to control and monitor possible sample cross-contamination during sample preparation. For example, a barren silica sand is submitted on a routine basis that requires pulverizing, in addition to the standard chemical analysis. The control chart for Cu and Zn (Figure 2) demonstrates that up to 540 ppm Cu and 650 ppm Zn may be contributed by sample cross-contamination. The problem is related to the occurrence of high-grade material in the sample suite, but cannot be specifically linked to incomplete cleaning of the pulverizers or solution carry-over during AAS analysis without additional investigations.

Sample cross-contamination during pulverizing has been investigated previously. Bloom (1993) analyzed barren silica sand that was milled immediately after high-grade sulphide samples were milled in the same equipment. The values reported for the silica sand were 1–6% of the value of the immediately preceding sample. The silica sand sample milled immediately after a sample containing 14.7% Cu and 2.9% Zn, reported 0.55% Cu and 0.10% Zn. The results of the study suggest that sample cross-contamination during pulverizing should be considered as a possible source of errors.

The quality control programme described was implemented for a drilling program designed to define an ore reserve. Potential problems,

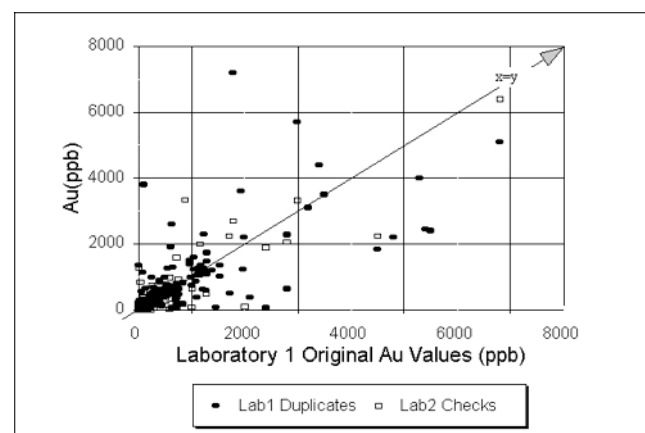
related to sample cross-contamination at several stages of preparation and analysis, could be controlled by submission of visibly high-grade material in batches separate from unmineralized samples. There would be additional logistical steps required to separate mineralized samples, at either the drill site or the core shack, but the effort would ensure that more reliable data were reported.

An additional mechanism for measuring the reproducibility of analytical data is the routine duplicate analysis of sample pulps and analysis of the same pulps at an alternative laboratory. A suite of data from frontier laboratories illustrates the difficulties in assessing the information. Figure 3 is a standard X-Y plot where two results generated by Laboratory 1 in the same batch are plotted against each other. The gold values do not reproduce well over the entire range of gold concentrations. Due to the poor reproducibility of the data, sample pulps were also submitted to a second laboratory (Laboratory 2). The checks by Laboratory 2 do not agree well with Laboratory 1 results; a bias between the two laboratories is not apparent.

The poor reproducibility of the gold results is primarily due to the inhomogeneous nature of the pulverized sample material. The degree of irreproducibility can be measured using Howarth-Thompson plots, variance analysis and experiments based on alternative sample preparation schemes (Hall and Bonham-Carter, 1988; Ramsey *et al.*, 1992; Thompson and Howarth, 1978). Several researchers have documented the importance of designing an appropriate sampling methodology (Burn, 1981; Clifton *et al.*, 1969; Gy, 1976).

For the two case histories presented, the mining companies must decide whether there is sufficient confidence in the data to calculate ore reserves, make a financing decision and convince potential investors of the merit of the property. Alternative sample preparation and analytical schemes should be considered to reduce the irreproducibility of the results. Any additional costs are justifiable on the basis of improved confidence in the data and the reduction in the risk associated with making decisions based on the data.

Similar risks are associated with interpreting the data from geochemical exploration surveys. In regional surveys, a sample mix-up in the laboratory could mean that a follow-up area would be selected based on (erroneous) anomalous geochemical results and a subsequent



**Figure 3:** Au concentrations determined in duplicate at Laboratory 1 and check analyses at Laboratory 2.

visit to the site would fail to confirm the anomalous values. The anomalous geochemical results should have been assigned to a different follow-up area, but that site was not revisited; mineralization at the site may remain untested.

Geochemical anomalies may be subtle and variations between sample batches could mask areas of mineralization. Monitoring the accuracy of analytical results by routine insertion of control samples will eliminate variations between sample batches. Laboratories can be requested to repeat analyses of sample batches where there are unacceptable results for control samples; these reanalyses are usually performed free of charge.

Precision should be measured, particularly where expected concentrations are near the detection limit of the analytical method. The analytical precision can be determined by reviewing the results for routine laboratory duplicates. Variations due to sample inhomogeneity or site variation can be measured by the insertion of field duplicates and sample preparation duplicates. Measurement of the variation will determine the confidence in the data set and provide guidelines for interpretation of subtle geochemical anomalies.

These examples of monitoring a base metal and gold project are from projects in frontier exploration regions. The challenges associated with operating a laboratory in these regions are more difficult than in North America, Australia and Europe. However, poor quality data may also be generated by experienced laboratories in countries with well developed infrastructures. Hall (1996) describes the results for fine-grained, homogeneous standard reference materials in a round robin conducted for the certification of precious metals. The range of values for three reference materials (TDB-1, WGB-1 and UMT-1) are presented in Table 2. The thousandfold range of Au values for WGB-1 is attributed to poor analytical procedures and quality control.

## CONCLUSIONS

Michael Thompson (1992) summarizes the reality of data quality. He says "All analytical data are based on measurements, and as such are inevitably prone to errors. Because of this we should in the first instance adopt a healthy scepticism about the quality of newly acquired data, whether they were produced by ourselves or by others. Until we have satisfied ourselves that our measurements are capable of supporting the interpretation that we wish to make, we should refrain from including them in our databases. If we cannot thus satisfy ourselves, then we must be prepared to reject the data or accept the consequences of an invalid interpretation."

The consequences of an invalid interpretation may range from not finding a new deposit during a regional reconnaissance program to overestimating the grade and tonnage of a deposit before making a commitment to large capital expenditures. Although all chemical data are prone to error, the challenges of operating in a remote, frontier location increases the probability that errors will occur. Typical problems include sample cross-contamination, high detection limits, analytical bias, sample mix-ups and long delays.

Precautions can be taken to ensure reliable data quality including:

1. laboratory audits and regular tours;
2. review of analytical procedures;
3. submission of standards, blanks and field duplicates;

**Table 2: Range of values in round robin.**

	Recommended	Minimum <sup>[1]</sup>	Mid. ICP-MS <sup>[2]</sup>	Max. FA-AAS
<b>Gold</b>				
TDB-1	6.3 ± 1.0	2.0	72	675
WGB-1	2.9 ± 1.1	1.3	52	2588
UMT-1	48 ± 2	26	104	549
<b>Palladium</b>				
TDB-1	22.4 ± 1.4	<10	70	716
WGB-1	13.9 ± 2.1	7	23	309
UMT-1	106 ± 3	53	164	284

1. Indicates that one lab using the identified method was responsible for this column of erroneously high concentrations

2. Indicates that various methods reported these low minimums.

4. personal communication with laboratory staff;
5. submission of check samples to a reference laboratory on a routine basis; and
6. contract specification that invoices are payable after evaluation of quality control data on a batch basis.

Some production-oriented laboratories have been accredited under ISO9000 guidelines and others are reviewing the costs and practicality of accreditation. Accreditation will provide clients with additional confidence in the consistent application of documented procedures but will not eliminate human error.

Although there are many risks associated with operating in frontier locations that cannot be controlled, the reliability of a geochemical laboratory can be measured and a potential risk eliminated.

## REFERENCES

- Bloom, L., 1993, Man-made parameters in elemental analysis: SME Pre-print 93-79: pp.5.
- Burn, R.G., 1981, Data reliability in ore reserve assessments: Mining Magazine, October, 289-299.
- Clifton, H.E., Hunter, R.E., Swanson, F.J., and Phillips, R.L., 1969, Sample size and meaningful gold analysis: United States Geological Survey Prof. Paper 625-C.
- Fletcher, W.K., 1981, Quality control in the laboratory, *in* Govett, G.J.S., ed., Analytical methods in geochemical prospecting: Handbook of exploration geochemistry, v.1, Elsevier, 25-46.
- Fletcher, W.K., 1987, Analysis of soil samples, *in* Fletcher, W.K., Hoffman, S.J., Mehrtens, M.B., Sinclair, A.J., Thomson, I., eds., Exploration geochemistry: Design and interpretation of soil surveys, (1987): Soc Econ Geol, 79-96.
- Garrett, R.G., 1969, The determination of sampling and analytical errors in exploration geochemistry: Econ. Geol., **64**, 568-571.
- Govindaraju, K., 1994, Compilation of working values and sample description of 383 geostandards: Geostandards Newsletter, **18**, pp. 1-158.

- Gy, P., 1976, The sampling of particulate materials—a general theory: Symposium on sampling practices in the mineral industries, The Australian Inst. of Mining and Metallurgy, Victoria, Australia, 17-33.
- Hall, G.E.M., 1996, Twenty-five years in geoanalysis, 1970-1996: *Jour Geochem Expl*, **57**, Nos.1-3, 1-8.
- Hall, G.E.M., and Bonham-Carter, G., 1988, Review of methods to determine gold, platinum and palladium in production-oriented laboratories, with application of a statistical procedure to test for bias: *Jour Geochem Expl*, **30**, 255-286.
- Hall, G.E.M., Vaive, J.E., Coope, J.A., and Weiland, E.F., 1989, Bias in the analysis of geological materials for gold using current methods: *Jour Geochem Expl*, **34**, 157-171.
- Hill, W.E., 1974, The use of analytical standards to control assaying projects: Vancouver IGES, 651-657.
- Howarth, R.S., Thompson, M., 1976, Duplicate analysis in geochemical practice, Part II: *Analyst* 101 (1206), 699-709.
- Kane, J.S., 1992, Reference samples for use in analytical geochemistry: their availability, preparation and appropriate use: *Jour Geochem Expl*, **44**, 37-63.
- Kretz, R., 1985, Calculation and illustration of uncertainty in geochemical analysis: *Jour Geol Educ.*, **33**, 40-44.
- Levinson, A.A., Bradshaw, P.M.D., and Thomson, I., 1987, Discrepancies in analytical determinations of gold, Arizona, U.S.A., *in* Levinson, A.A., Bradshaw, P.M.D., Thomson, I., eds., *Practical problems in exploration geochemistry*: Applied Publishing, 148-149.
- Plant, J.A., 1973, Random numbering system for geochemical samples: *IMM Trans.*, **82**, B64-B65.
- Plant, J.A., Jeffrey, K., Gill, E., and Fage, C., 1975, The systematic determination of accuracy and precision in geochemical exploration data: *Jour. Geochem. Expl.*, **4**(4), 467-486.
- Potts, P.J., Tindle, A.G., and Webb, P.C., 1992, *Geochemical reference material compositions: Rocks, minerals, sediments, soils, carbonates, refractories and ore used in research and industry*: CRC Press Inc.
- Ramsey, M.H., Thompson, M., and Hale, M., 1992, Objective evaluation of precision requirements for geochemical analysis using robust analysis of variance: *Jour. Geochem. Expl.*, **44**, 23-36.
- Thompson, M., 1983, Control procedures in geochemical analysis, *in* Howarth, R.J., ed., *Statistics and data analysis in geochemical prospecting: Handbook of exploration geochemistry*, v.2, Elsevier, 39-58.
- Thompson, M., 1992, Data quality in applied geochemistry: the requirements and how to achieve them: *Jour. Geochem. Expl.*, **44**, 3-22.
- Thompson, M., and Howarth, R.J., 1978, A new approach to the estimation of analytical precision: *Jour. Geochem. Explor.*, **9**, 23-30.