

APPENDIX 5. QUALITY ASSURANCE AND QUALITY CONTROL (QA/QC) OF GEOCHEMICAL AND MINERAL ANALYSES

INTRODUCTION

The samples and field data (including field observations and measurements) are the basic component of the data collection and interpretation, which ultimately leads to the project conclusions. Therefore, it is important to understand the spatial and geological context and to describe the types of samples collected, sample preparation, and sample analyses. The purpose of this appendix is to present data to support the accuracy and precision for the geochemical (Appendix 3) and mineralogical analyses obtained by NMBGMR. The data were obtained from the various laboratories and at least 10% of the data were validated or checked by an additional staff member to assure the data were entered into the database properly. If during validation, data were found to be entered incorrectly, the error was immediately corrected. This report only describes the sample collection and preparation of samples collected during the project. The QA/QC procedures for the electron microprobe laboratory at NMIMT are explained at <http://geoinfo.nmt.edu/labs/microprobe/home.html> (accessed 1/6/2019).

A *sample* is a representative portion, subset, or fraction of a body of material representing a defined population (Koch and Link, 1971; Wellmer, 1989; Rollinson, 1993; Davis, 1998; Schreuder et al., 2004; Neuendorf et al., 2005; Downing, 2008). A sample is that portion of the population that is actually studied and used to characterize the population. Collecting a representative sample of rock-pile material can be difficult because of the compositional, spatial, and size heterogeneity of the material. It also is necessary to define the particle-size fraction of the sample required and analyzed, because of the immense size heterogeneity in many rock piles (Smith et al., 2000). The sampling process is summarized below:

- Define the sample population
- Define the parameters to be measured
- Define the number of samples to be collected and where
- Define the sample collection method
- Define the quantity of sample collected
- Collect the sample
- Record field observations and sample description
- Review the sampling process and modify if needed.

The determination of total error of a measurement depends upon several parameters, including the sample error and analytical error (Rollinson, 1993; Schreuder et al., 2004). The sample error is the error that results from studying the collected sample instead of the entire population and depends upon completeness, comparability, and representativeness, as defined below:

- *Completeness*—the comparison between the amount of valid, or usable, data originally planned to collect, versus how much was collected.
- *Comparability*—the extent to which data can be compared between sample locations or periods of time within a project, or between projects.
- *Representativeness*—the extent to which samples actually depict the true condition or population being evaluated

Sample error is the error caused by observing a sample instead of the whole population and typically is dependent upon the sample-to-sample variation and is controlled by collecting a sample of suitable size relative to the heterogeneity of the sampled material, as well as a sufficient number of samples to characterize the population (Wellmer, 1989).

Basically, all analytical measurements are incorrect at some level and are measured against an agreed upon standard of analysis. It is just a question of how large the errors are compared to an agreed upon standard of accuracy and if those errors are acceptable; these are typically defined in the original sampling plan. Analytical error is the error that results from laboratory analysis, is typically reported by the laboratory, and is defined by precision and accuracy, as defined below:

- *Precision* is the degree of agreement among repeated measurements of the same characteristic and is monitored by multiple analyses of many sample duplicates and internal standards. It can be determined by calculating the standard deviation, or relative percent difference, among samples taken from the same place at the same time (i.e. duplicates and triplicates, Fig. 1).
- *Accuracy* measures how close the results are to a true or accepted value and can be determined by analyzing certified reference standards as unknown samples and comparing with known certified values (Fig. 1).

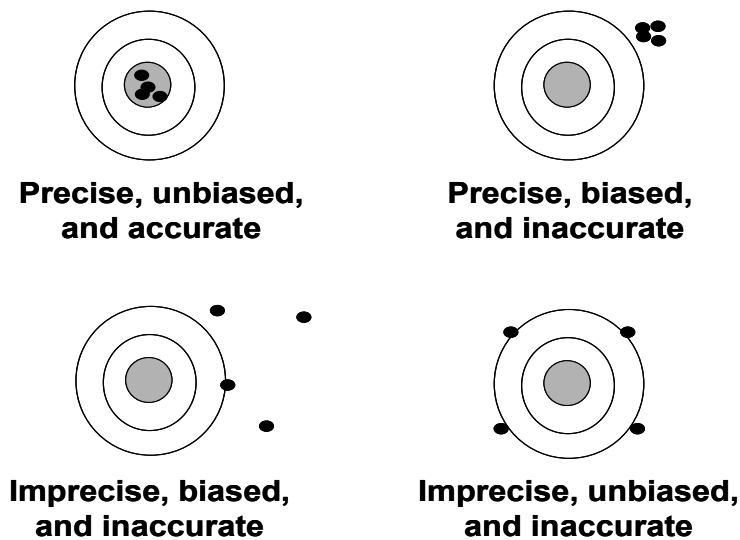


FIGURE 5-1. Diagram illustrating the difference between precision, bias, and accuracy.

FIELD PROCEDURES

A standardized protocol was followed for sample collection. Different sampling strategies were employed based upon the purpose of each sampling task. Typically, at each site a grab, or bulk rock sample or other material was collected for petrographic study and geochemical analyses. A hand specimen was collected from some sites for thin section analysis. Each sample was stored in a separate bag or bucket, assigned a unique number (Table 2, 3, Field ID), logged on a field description form (Appendix 3), and entered into the

project database. Selected sample sites were marked in the field and a digital photograph was taken at most localities. Photographs provide visual record of the sample site (Table 3). The photograph form identified site specifics, provided basic location and other data about the photograph (SOP 4). Location information obtained by global positioning system (GPS, SOP 3), type of sample, and field petrographic descriptions were collected. Geologic observations were recorded on the field description form and each site was located on a map, if possible (SOP 5). Hand specimen description provided a record of what was collected, which aided in petrographic descriptions and provided information on the sample for the laboratory analysis (for example, high pyrite samples may be treated differently than low pyrite samples). The hand specimen description was the preliminary data used to determine what samples required additional analyses. Several different types of samples were collected:

- Outcrop samples of unweathered (or least weathered) igneous rocks
- Outcrop samples of weathered igneous rocks
- Samples of the vein material within altered host rocks
- Dump samples of mines and prospects.

We used two types of standards: certified standards and internal standards. The laboratories used certified standards, which are commercial standards with certified values as determined by round robin analyses at numerous certified laboratories. The certified standards are expensive, so we submitted internal standards. The internal standards are samples we collected and analyzed by different methods and over several years' time. Numerous duplicates and triplicates were submitted blind to the laboratory and analyzed with each sample batch to compare and assess analytical precision, accuracy, and representativeness. Detection limits vary between laboratories and even samples. Uncertainty of analyses is generally <5% of duplicate samples and standards that were analyzed.

Additional data used in this report were compiled from previous data sets and published reports as indicated in Table 5-1. Additional information can be found at the websites of Activation Laboratories (methods for which can be found at <https://cdn.actlabs.com/wp-content/uploads/2019/10/Actlabs-Schedule-of-Services-Canada-2019-07-22.pdf> <https://actlabs.com/geochemistry/lithochem-and-whole-rock-analysis/>) and ALS Laboratories (methods for which can be found at https://www.alsglobal.com/en-us/?gclid=EAIaIQobChMI9rrc5an05gIVFq5kCh3n1AEBEAYASAAEgLbY_D_BwE).

TABLE 5-1. Summary of laboratory chemical analyses of different data sets of samples used in this report (Appendix 3). See references for more information on sample preparation, chemical analyses and detection limits. Abbreviations are defined in the text.

Data set	Sample numbers	Laboratory	Elements	Analytical method	Comments
Schreiner (1994)	1-35	Bondar Clegg, Inc., Lakewood, Co.	REE, Sc, Th, U Au Sb, As, Bi, Cr, Co, Cu, Pb, Fe, Mn, Mo, Ni, Ag, W, Zn, Ba, Sr, Y, Nb, Hg, Te	INAA; Fire assay-AAS; Specific ion probe; ICP-AES; XRF; Cold vapor AAS; AAS; Borate plasma emission spectroscopy	Not all samples were analyzed for major elements and important trace elements (F, etc.)

Data set	Sample numbers	Laboratory	Elements	Analytical method	Comments
			Major elements F		
This report	Various samples prefixed by CORN	USGS laboratory	Major elements Trace elements Loss on ignition (LOI) F	WDXRF; ICP-AES-MS; Gravimetric; Ion chromatograph	
Texas Bureau of Economic Geology	Samples prefixed by CND	USGS laboratory	Major elements Trace elements Loss on ignition (LOI)	WDXRF; ICP-AES-MS; Gravimetric; Ion chromatograph	
This report	Various samples prefixed by CORN	ALS, Reno, NV	Major elements Trace elements Loss on ignition (LOI) F	XRF; ICP-AES-MS; Gravimetric; Ion chromatograph	Some samples from ALS are reported as upper detection limits (Ba, Sr, Cu, etc.)
Geovic Mining Co. samples	various		Major elements Trace elements Loss on ignition (LOI) F	XRF; ICP-AES-MS; Gravimetric; Ion chromatograph	

Samples collected in the field were selected and prepared for specific laboratory analyses, then sent to a laboratory for analyses. Some samples were sent to USGS laboratories and that data was verified by the USGS using known QC samples, duplicate analyses and other QA/QC procedures that are part of the routine USGS approved process. Samples were collected at the surface. Surface samples were dried, crushed, split, and pulverized according to standard ALS Laboratory Group preparation methods PREP-31. Samples were analyzed by ALS Laboratory Group for major and trace elements by a variety of analytical methods (CCP-PKG03 and Au-ICP21), including X-Ray Fluorescence (XRF), inductively coupled plasma atomic emission spectroscopy (ICP-AES), and inductively coupled plasma mass spectrometry (ICP-MS). This method combines the whole rock package ME-ICP06 plus carbon and sulfur by combustion furnace (ME-IR08) to quantify the major elements in a sample. Trace element analyses, including the full REE suite, are performed after a choice of three digestions and either an ICP-AES or ICP-MS finish: 1) a lithium borate fusion for the resistive elements (ME-MS81), 2) a four acid digestion for the base metals (ME-4ACD81) and 3) an aqua regia digestion (ME-MS42). Gold was analyzed separately using fire assay with an ICP-MS finish (Au-ICP21).

METHOD SUMMARIES

Samples were shipped by U.S. Postal Service to USGS or ALS Laboratory Group. Not all samples collected were analyzed. Samples were collected at the surface. A summary of procedures is found in the main report.

Major elements are determined in rocks by wavelength dispersive X-ray fluorescence (WDXRF or XFR). The sample is fused with lithium metaborate/lithium tetraborate flux and the resulting glass disk is introduced into the WDXRF and irradiated by an X-ray tube. Loss on ignition (LOI) is measured by gravimetric methods.

Trace elements are determined in rocks, minerals, and soils after they are fused at 750°C with sodium peroxide and the fusion cake dissolved in a dilute nitric acid. The resulting solution is analyzed by ICP-OES and/or ICP-MS.

X-ray fluorescence (XRF) Analyses

The sum of major oxides (including SO₃) should total between 98 and 101% (Appendix 3), however, many samples have lower or higher totals. Extreme totals are found mostly in mineralized samples, especially samples with high F, Ba, Pb, or Cu.

The precision of analyses is acceptable (within 10%) for samples where multiple analyses of the same sample were obtained (Table 5-2). For every 10 samples submitted, a duplicate sample was analyzed; these analyses compared within 10% (see project database for additional data).

There are numerous reasons why duplicate samples and standards do not always reproduce precisely. Some samples, such as rhyolite and basalt, grind into a powder more easily than other samples, such as stream-sediment samples and nepheline syenites. Fusion techniques required for XRF analyses vary from lab to lab and also can differ between different personnel that could result in variations between sample pairs. Analytical error is higher for analyses with concentrations close to the detection limit. In addition, dump samples and alluvium are very heterogeneous and difficult to completely homogenize. Most variations between duplicate samples are probably a result of sample inhomogeneities and analytical errors related to low concentrations. Another problem encountered with dump samples is the variability of sample collection.

ACCURACY AND PRECISION OF ROCK CHEMISTRY DATA (SOLIDS)

The accuracy of the data is how close the measured value is to the true or accepted value. Analyzing certified standards as unknown samples and comparing these values with certified values can monitor accuracy. Each laboratory is responsible for the accuracy of the data they produce, and the laboratory's QA/QC protocols are available upon request from the project manager. Precision is the degree of agreement among repeated measurements of the same characteristic and monitored by multiple analyses of many sample duplicates and internal standards. It can be determined by calculating the standard deviation, or relative percent difference, among samples taken from the same place at the same time (i.e. duplicates and triplicates). In general, analyses obtained from the laboratories are in agreement with certified values of certified standards and precision is excellent between multiple analyses (see documentation in sections below).

However, differences between certified standards and duplicate pairs do exist. Generally, no corrective procedures could be applied to solid samples. Variation in preparation of the glass disk used in the analysis is a major cause of these differences (Johnson et al., 1999). Nugget effects can account for variations in copper (Cu), iron (Fe), lead (Pb), sulfur (S), zinc (Zn), and zirconium (Zr), observed in some pairs of samples. An example of the nugget effect is where a small grain of native gold or other mineral occurs in one split and not the other split and thus produces a higher concentration. Another variation between certified values and the results provided by the laboratories is a result of different analytical techniques. ICP requires acid digestion and analysis of a liquid-based solution. In some cases, not all of the solid will be completely digested and

can result in a lower value than that obtained by certified values generated using XRF or instrumental neutron activation analysis (INAA).

The sum of major oxides should total between 99 and 101% (Appendix 3). Samples of NMBGMR on-going standards were analyzed for most batches and the difference between analyses is acceptable, within 10% (Table A5-1). The precision of analyses is acceptable (within 10%) for samples where multiple analyses of the same sample were obtained (Table A5-1). For every 10 samples submitted, a duplicate sample was analyzed; these analyses compared within 10%.

SUMMARY

Samples were collected, prepared, and analyzed according to standard methods for each specific laboratory analysis. Samples are archived at the NMBGMR. Samples collected are complete, comparable, and representative of the defined population at the defined scale. Precision and accuracy are measured differently for each field and laboratory analysis (parameter). Most geochemical laboratory analyses depend upon certified reference standards and duplicate or triplicate analyses. Effective sampling and analysis helps plan the field program and the control of accuracy and precision. This provides a large, high-quality set of observations and measurements that are adequate to support the interpretations and conclusions of this report. Field and laboratory audits by the senior author were performed to ensure that procedures were followed.

REFERENCES

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