Appendix I: Lithogeochemical Surveys

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Stephen J. Piercey obtained his B.Sc. (Hons) and M.Sc. degrees from Memorial University of Newfoundland (Canada) and a Ph.D. from the University of British Columbia (Canada). He has held positions as Assistant and Associate Professor in the Department of Earth Sciences and Mineral Exploration Research Centre at Laurentian University and has worked as a full-time consulting geologist and the principal of SJPGeoConsulting. Currently Stephen is a University Research Professor at Memorial University and Adjunct Professor at Laurentian. His interests integrate field- and laboratory-based studies on the genesis of mineral deposits and the tectonic evolution of mountain belts, with emphasis on volcanogenic massive sulphide (VMS), orogenic Au, and U deposits. His latest research has focused on the larger scale tectonic and magmatic settings of VMS deposits, with an emphasis on their volcanic, sedimentary, and hydrothermal reconstruction; sources of metals, fluids, and sulphur; and their relationship to the evolution of the lithosphere, hydrosphere, atmosphere, and biosphere. Dr. Piercey has been awarded the Lindgren Medal (SEG), Gross Medal (MDD-GAC), Past President's Memorial Medal (CIM), Howard Street Robinson Medal (GAC), and Hutchison Medal (GAC). He is a Professional Geoscientist (PGeo) in Newfoundland and Labrador (PEGNL) and Ontario (PGO), Canada.

Contextual Information

Many deposits are hosted in igneous rocks (e.g. volcanogenic massive sulphide (VMS), porphyry Cu, greenstone orogenic Au), and these rocks can provide critical information about primary igneous processes, including chemostratigraphy (e.g. VMS deposits: Piercey 2011), magmatic evolution and redox features of magmas (e.g. porphyry Cu: Richards et al. 2012), and/or potentially chemically reactive rocks (e.g. orogenic Au: Ropchan et al. 2002). These rocks can also undergo fluid-rock interactions and may provide a hydrothermal footprint from which specific elements and element ratios can be used to vector towards mineralization. This appendix is focused on the utilization of igneous rocks in exploration geochemistry, including the lithogeochemistry of volcanic and intrusive rocks for understanding (1) the primary lithogeochemical signatures related to primary igneous process, and (2) any secondary, hydrothermal alteration-related signatures related to fluid-rock interaction associated with deposit-forming processes (i.e. the hydrothermal footprint of mineralization).

Samples for lithogeochemical surveys are typically acquired for geological mapping, deposit reconstructions, stratigraphic studies, and regional reconnaissance. Providing an adequate geological context for the samples, namely the stratigraphic and structural setting, and the location within the hydrothermal alteration and mineralization environment, as appropriate, is critical component.

Within this framework, key questions and/or hypotheses to be investigated by the sampling survey should be articulated and documented in the subsequent lithogeochemical report.

Sampling

Instructions to samplers

Ideally, instructions for the samplers should be provided in a hands-on training exercise in the field and/or in a core shack. Written documentation should also be provided outlining the standard sampling protocols and in-field sample preparation and a copy should be placed in the core shack, and/or field camp, and on a company server. These instructions will need to be updated for each project or circumstance.

Sample locations

It is important to record adequate information about the sample sites, especially the location (ideally determined using GPS) and any uncertainties in location measurements. For surface samples, additional details about the site physiography, vegetation, quality of outcrop, location on local grids, and other information deemed relevant should be included. For drill core samples, which are usually collected in a core shack and/or core storage area, the drill hole location and the depth and length of the sample should be noted. In a mine environment, the location within the local mine grid, underground mine slot, or other position underground should be recorded.

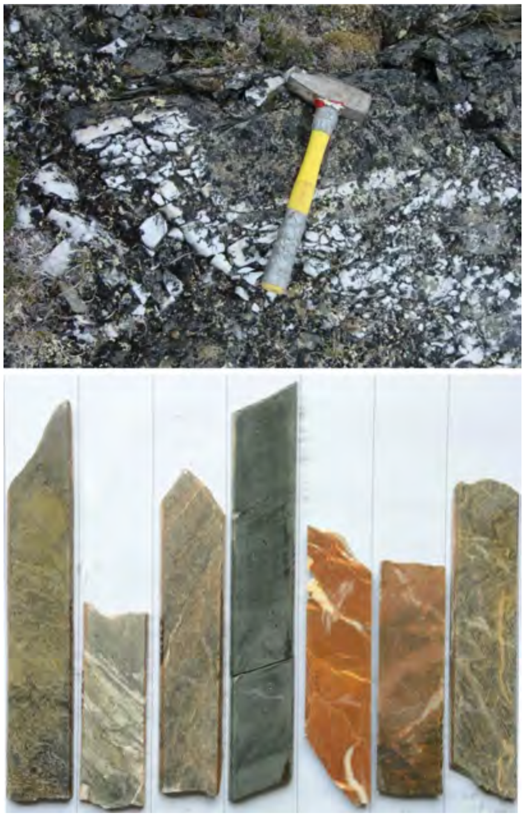
Sampling equipment and supplies

The equipment and supplies used for the project should be documented in the report, including the following key information:

- sample location equipment used (e.g. GPS, topographic maps, satellite images, portable tablet for direct GIS input);
- types of rock hammers and related equipment used for procuring samples;
- size and types of sample bags for storing and transporting samples;
- types of sample tags for recording in-field information and how these tags are included with the samples (e.g. inside the bag);
- details of how the samples were secured after being placed in sample bags (e.g. zip-tied or other security measures taken);
- the nature of any other containers used for shipping the samples to the laboratory (e.g. rice bags, rock buckets).

Sampling procedures

Sampling protocols for lithogeochemical surveys should be



Due to the potential for sample heterogeneity, it is important to specify in the report the sub-sampling rules and guidelines that were followed.

clearly documented in the report. For surveys aimed at understanding primary igneous processes (e.g. chemostratigraphy in VMS deposits, intrusion chemistry and petrology in porphyry Cu-Mo-Au deposits) the logic and reasoning behind why samples were collected, units of measure (e.g. volume, weight), and other criteria should be recorded. Similarly, for alteration studies, the alteration intensity and assemblage should be documented. For both types of studies, the spatial distribution of the samples should be documented and the reasoning for the distribution discussed (e.g. *n* samples per km; every *n* metres in drill core; other mineralogical or textural criteria).

Sample notes

The following information should be recorded for each sample:

- date of collection;
- sample number;
- name(s) of the sampler(s);
- sample location, including the coordinate information and the coordinate system;
- outcrop quality;
- stratigraphic and structural relationships;
- approximate dimensions of the sample;
- for diamond drill core samples, the core type (e.g. NQ, BQ), the location, depth of the sample (e.g. from x to y = sample length), and whether it is full, half, or quarter core;
- rock type and subtypes;
- dominant alteration minerals, alteration assemblages, and intensity of alteration (e.g. pervasive versus patchy).

Additional general notes should always be kept and stored in a digital archive but it may not be necessary to include these in the report.

Field duplicates and insertion of field blanks

If field duplicates are collected, the reasoning for the duplicates, the frequency of collection, and descriptive details of the duplicate sample relative to the original sample should be recorded. Duplicates from drill core may involve split core and it is critical to document the size of the core and how much core was utilized in the original and the duplicate samples (e.g. half core versus quarter core). If a field blank is used, a description of the blank should be included, the reason the blank was chosen, and the frequency of insertion should be reported.

Final (in-field) sample preparation

Any additional measurements taken from the samples (e.g. density, magnetic susceptibility) should be recorded.

It is also very important to document the chain-of-custody steps taken during final sample preparation and transport to the laboratory (e.g. bag types, tags and their location with the sample, zip ties or other security measures, courier or personnel used for transportation and how samples were tracked).

Insertion of Quality Control

Quality control protocols should include field and analytical duplicates, blanks, and reference materials (*see* review by Piercey 2014, and references therein) and must be included in the report. The following are key points that should be documented in the report:

- the frequency of field duplicates and field blanks (*see* additional information above);
- the source and nature and of certified reference materials (CRMs)(in powder form), the reason for the choice of the CRM, what analytes the CRM is monitoring (for precision and accuracy), and the frequency of insertion should all be reported;
- for blanks in powder form, the type of material submitted, what analytes the blank is being used to monitor, the range in concentration of the analytes in the blank, and the frequency of insertion should be reported.

Sample Preparation

The documentation of sample preparation and dissolution methods is critical for lithogeochemistry. Information that should be documented includes the following:

- whether or not field samples have had the weathered edges removed and if so, how this was done (e.g. in the field with a hammer or post-fieldwork using a saw);
- type and nature of the saw used to cut the samples (e.g. water- versus oil-cooled: the latter should be avoided) and the cleaning protocols followed between samples (e.g. was the saw blade and surface cleaned with water between samples

to minimize carry-over contamination?);
- how samples were crushed and pulverized:
  - the nature of the crusher and riffler (e.g. steel, ceramic);
  - the choice of mill for pulverizing should be documented (e.g. agate versus mild (carbon) steel versus tungsten carbide: avoid the latter mill, if possible);
  - an estimate of the final size (in microns or mesh) of the powder after pulverizing;
  - cleaning protocols between crushing, riffling, and pulverizing.

Laboratory Analysis

The sample preparation and analytical instrument finish should be discribed in the report. In particular, the following information should be recorded.

- The sample preparation steps and types of dissolutions utilized. For example, in lithogeochemical studies it is common to fuse the sample powder (e.g. with lithium metaborate or Na_2O_2), followed by dissolution of the fused material in one or more acids. This is done to ensure that immobile elements, which are used for primary igneous studies and are found in highly resistant minerals like zircon, monazite, and chromite (e.g. HFSE, REE, Cr), are completely recovered and the resistant minerals completely dissolved. For mobile elements, which are commonly utilized for defining a hydrothermal footprint (e.g. base metals, precious metals, metalloids), partial digestions, such as four acid (HF-HNO_3-HCl-$HClO_4$), three acid (HF-HNO_3-HCl), and aqua regia are often used. In some cases, no dissolution methods are used (e.g. XRF, INAA); in which case, document the sample preparation procedures prior to analysis.
- If precious metals were determined, such as Au or platinum group elements (PGE), provide details of the assay method and the instrument utilized for the analytical finish.
- For each step in sample preparation, provide the weight of the powdered material that was used for each step as well as the analytical method used.
- Provide details of the instrumentation utilized to determine the concentrations of the elements. If possible, the details (e.g. manufacturer, model) of the specific instruments should be included.
- Ideally, for each suite or group of elements included in tables in the report, the dissolution method and analytical instrument should be written next to the element being presented (i.e. SiO_2 (FUS-ICP-ES), Au (FA-ICP-ES)).
- If elements have been determined by multiple methods and/or instruments, it is critical to identify and document which method is preferred for each of the elements. If data from multiple methods are used (e.g. for varying concentrations), the threshold or other criteria used for element reporting should be provided.

Using field-portable analytical devices, such as a hand-held XRF, have the advantage of speed, cost savings and convenience; however, reduced accuracy and precision as well as limited elements that can be detected make them a semi-quantitative device and generally unsuitable for most lithogeochemistry.

- In some cases, real-time measurements may be obtained using instruments such as a portable XRF (pXRF). In which case, the following should be documented:
  - the type of instrument (manufacturer and model);
  - the type of X-ray tube;
  - the mode of data acquisition (often referred to as soil versus mining modes);
  - the length of time for data acquisition;
  - whether sample pulps or rocks/core were analyzed;
  - how many points were analyzed per sample;
  - any quality assurance/quality control (QA/QC) materials and results.

Petrochemical work often results in the total destruction of the existing minerals. Fusion into a glass is often required and commonly the most trusted method.

Data Presentation

Methods of presenting lithogeochemical data are diverse and the choice is dependent on the problem being investigated and the nature of the survey; however, there are basic methodologies that can be used and presented in geochemical reports, including the following:

- Multivariate statistical methods (e.g. principal component analysis, K-means cluster analysis) can be used to evaluate elemental variability and high-level correlations within the data set.
- Primary lithogeological classification can be used to classify rocks and evaluate various igneous attributes:
  - alkalinity (e.g. total alkali versus silica diagrams (TAS): Cox et al. 1979; Middlemost 1994); Winchester and Floyd/Pearce plots (Winchester and Floyd 1977; Pearce 1996);
  - magmatic affinity diagrams (e.g. determining the magma series – tholeiitic, transitional, calc-alkalic utilizing Zr-Y, Th-Yb, La-Yb ratios: Ross and Bedard 2009);
  - multi-element normalized diagrams (e.g. chondrite and primitive mantle normalized plots of rare earth elements and other trace elements);
  - fractionating igneous phases (e.g. using trace elements via binary plots such as Pearce element ratios: Pearce 1968);
  - perspectivity plots that are specific to the deposit type (e.g. FI-FIV rhyolite classification for VMS: Hart et al. 2004; Sr/Y-Y for porphyry Cu deposits: Richards et al. 2012).
- Evaluation of alteration attributes:
  - basic binary plots of mobile elements;
  - deposit-specific alteration indices and associated plots (e.g. an alteration box plot: Large et al. 2001);
  - various element and molar element ratios that are related to specific alteration minerals;
  - Pearce element ratio and general element ratio plots to test various alteration minerals and processes (e.g. Stanley and Madeisky 1994).
- Spatial evaluation of data:
  - map-level plots with various parameters presented in GIS software to illustrate spatial distribution (bubble plots, magmatic affinities, etc.);
  - downhole profiles of the various attributes above, including raw data, rock classification parameters, alteration indexes, etc.;
  - 2-D (i.e. sections) and 3-D maps of drill core results showing various elements and element ratios and patterns to evaluate the chemostratigraphy and primary igneous variations and the hydrothermal footprints of the mineralization.

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