Quantitative Mineral Mapping of Drill Core Surfaces I:  
A Method for µXRF Mineral Calculation and Mapping of Hydrothermally Altered,  
Fine-Grained Sedimentary Rocks from a Carlin-Type Gold Deposit  

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Abstract

Mineral distributions can be determined in drill core samples from a Carlin-type gold deposit, using micro-X-ray fluorescence (µXRF) raster data. Micro-XRF data were collected using a Bruker Tornado µXRF scanner on split drill core samples (~25 × 8 cm) with data collected at a spatial resolution of ~100 µm. Bruker AMICS software was used to identify mineral species from µXRF raster data, which revealed that many individual sample spots were mineral mixtures due to the fine-grained nature of the samples. In order to estimate the mineral abundances in each pixel, we used a linear programming (LP) approach on quantified µXRF data. Quantification of µXRF spectra was completed using a fundamental parameters (FP) standardless approach. Results of the FP method compared to standardized wavelength dispersive spectrometry (WDS)-XRF of the same samples showed that the FP method for quantification of µXRF spectra was precise (R² values of 0.98–0.97) although the FP method gave a slight overestimate of Fe and K and an underestimate of Mg abundance. Accuracy of the quantified µXRF chemistry results was further improved by using the WDS-XRF data as a calibration correction before calculating mineralogy using LP. The LP mineral abundance predictions were compared to Rietveld refinement results using X-ray diffraction (XRD) patterns collected from powders of the same drill core samples. The root mean square error (RMSE) for LP-predicted mineralogy compared to quantitative XRD results ranges from 0.91 to 7.15% for quartz, potassium feldspar, pyrite, kaolinite, calcite, dolomite, and ilillite.

The approaches outlined here demonstrate that µXRF maps can be used to determine mineralogy, mineral abundances, and mineralogical textures not visible with the naked eye from fine-grained sedimentary rocks associated with Carlin-type Au deposits. This approach is transferable to any ore deposit, but particularly useful in sedimentary-hosted ore deposits where ore and gangue minerals are often fine grained and difficult to distinguish in hand specimen.

Introduction

Understanding the distribution of minerals within ore deposits is important to determine the mineralization and alteration paragenesis, recognize the distribution and type of ore minerals, and understand how mineralogy influences ore processing (e.g., silicate mineral abundances; Johnson et al., 2019). Large-scale mineralogical studies have shown to be of great value in recent years with the advent of mineral mapping technologies, such as infrared spectrographic imaging and quantitative scanning electron microscopy (qSEM; Gottlieb, 2008). Understanding mineral distributions in rocks is of particular value to the mineral industry, where ascertaining the distribution of mineral species in a deposit could be beneficial to defining mineral resources, or more efficiently processing ore. Micro-X-ray fluorescence (µXRF) scanning is a relatively new analytical tool that allows chemical mapping of rock samples at a very fine scale (<100 µm), yet on sample sizes that lie between traditional SEM thin-section observations (< ~1 mm) and the core-scale observations made during logging and assay chemistry (~1 mm to m). Examples of applications of geochemical analyses using µXRF include studies of volcanicogenic massive sulfides (Genna et al., 2011), shale-hosted uranium (Xu et al., 2015), greenstone-hosted Cu-Co-Au (Fox et al., 2019), and environmental sciences (Croudace and Rothwell, 2015; Flude et al., 2017). In each of these studies, µXRF is used to visualize and, in some cases, quantify (Flude et al., 2017) the distribution of elements over the surface of mineral and rock samples, which in turn reveals textures and patterns that cannot be observed in hand samples. These chemical data, as shown here in this research, can also be interpreted in terms of mineral species.

The rocks analyzed in this study were selected from seven drill holes arranged in a transect (Fig. 1, Table 1) across hydrothermally altered and unaltered Paleozoic passive margin carbonate, carbonaceous shales, and siliciclastic rocks (Stewart, 1980) of the Fourmile Carlin-type Au discovery in Nevada. Mineralogy of Carlin-type deposits can be difficult to identify in hand specimen or thin section due to their fine-grained nature (Muntean, 2018). It is difficult to use shortwave infrared spectroscopy to identify minerals in the rocks which host Carlin-type gold deposits, because of the fine-grained samples and the lack of reflectance (Ahmed et al., 2010; Barker, 2017). In this study we show that µXRF can be used to accurately quantify elemental abundances.
via a fundamental parameters (FP) method by comparing FP results of rock samples with traditional whole-rock geochemistry analyses (WDS-XRF and 4-acid digest methods). In addition, quantified µXRF chemistry results can be further improved by calibrating FP results from rock powders with WDS-XRF results collected from the same rock samples. Finally, we demonstrate two methods for mineral identification and quantification using µXRF raster maps. The first method is a demonstration of the utility of the Bruker AMICS software (Bruker, 2018a) for mineral identification from µXRF spectra through a combination of XRF spectra library matching and clustering algorithms. For the second method we show that µXRF spectra can be accurately quantified and used to predict and map the quantitative mineral abundance across samples using a linear programming (LP) approach.
Table 1. List of Samples Used for XRF-WDS, Whole-Rock Geochemistry, QXRD, and μXRF (chemical maps and quantitative extractions) Analyses with Brief Description of Lithology and Alteration Type (numbers in the μXRF [quant] and XRF-WDS columns represent the number of subsamples taken from different areas of the core sample).

| Drill hole | Sample   | Depth (m) | μXRF (map) | μXRF (quant) | XRF-WDS | Whole rock | QXRD | MLA | Rock description |
|------------|----------|-----------|------------|--------------|---------|------------|------|-----|------------------|
| FM16-01D   | M180059  | 535.38    | 1          | 1            | x       | x          | x    | x   | Silicified, decalcified, and sulfidized argillitic carbonaceous mudstone |
| FM16-01D   | M180062  | 609.37    | x          | 1            | 1       | x          | x    | x   | Silicified and brecciated limey carbonaceous mudstone with illite enrichment |
| FM16-01D   | M180065  | 745.91    | 2          | 2            | 2       | x          | x    | x   | Pervasively sulfidized and argillized limey mudstone fault rock |
| FM16-01D   | M180069  | 863.44    | 2          | 2            | x       | x          | x    | x   | Limestone with minor silicification and argillization |
| FM16-07D   | M180074  | 1071.59   | 2          | 2            | x       | x          | x    | x   | Sulfidized and argillized muddy limestone |
| FM16-07D   | M180077  | 706.53    | 2          | 2            | x       | x          | x    | x   | Metacarbonate breccia with silicified clasts |
| FM16-07D   | M180080  | 823.48    | x          | 1            | 1       | x          | x    | x   | Limey mudstone with silica replacement front |
| FM16-07D   | M180083  | 906.48    | 1          | 1            | x       | x          | x    | x   | Dolomitic metacarbonate |
| FM16-07D   | M180088  | 1118.07   | 1          | 1            | x       | x          | x    | x   | Base metal vein-bearing marl with minor silicification |
| GRC-0427D  | M180093  | 685.69    | 2          | 2            | x       | x          | x    | x   | Metacarbonate with pinstripe pyrite and minor silicification |
| GRC-0427D  | M180095  | 715.11    | x          | 2            | x       | x          | x    | x   | Pervasively argilized limey mudstone with minor sulfidation and silicification |
| GRC-0427D  | M180097  | 736.20    | 1          | 1            | x       | x          | x    | x   | Carbonaceous limey mudstone breccia |
| GRC-0427D  | M180098  | 736.71    | 1          | 1            | x       | x          | x    | x   | Pervasively dolomitized limey mudstone |
| GRC-0427D  | M180099  | 764.50    | 1          | 1            | x       | x          | x    | x   | Muddy limestone with minor silicification and argillization |
| GRC-0427D  | M180101  | 823.05    | 1          | 1            | x       | x          | x    | x   | Muddy limestone with minor silicification and argillization |
| GRC-0427D  | M180102  | 877.00    | 1          | 1            | x       | x          | x    | x   | Muddy limestone with minor silicification and argillization |
| GRC-0427D  | M180104  | 925.07    | 1          | 1            | x       | x          | x    | x   | Mineralized limey mudstone breccia with pervasive silicification and sulfidation |
| GRC-0436D  | M180109  | 520.93    | 2          | 2            | x       | x          | x    | x   | Argillitic carbonaceous mudstone |
| GRC-0436D  | M180118  | 765.20    | 2          | 2            | x       | x          | x    | x   | Muddy limestone with minor silicification and argillization |
| GRC-0432D  | M180121  | 200.62    | 1          | 1            | x       | x          | x    | x   | Weathered carbonaceous limey mudstone with minor argillization and silicification |
| GRC-0432D  | M180123  | 296.27    | 1          | 1            | x       | x          | x    | x   | Carbonaceous limey mudstone |
| GRC-0432D  | M180127  | 420.29    | 1          | 1            | x       | x          | x    | x   | Limestone |
| GRC-0432D  | M180130  | 555.04    | x          | 2            | 2       | x          | x    | x   | Limey mudstone with silica replacement front and sulfidation |
| GRC-0432D  | M180136  | 814.09    | 1          | 1            | x       | x          | x    | x   | Muddy limestone |
| GRC-0428D  | M180145  | 763.86    | 1          | 1            | x       | x          | x    | x   | Metacarbonate with minor silicification and sulfidation |
| GRC-0430D  | M180152  | 654.50    | 2          | 2            | x       | x          | x    | x   | Marble |
| GRC-0430D  | M180157  | 855.42    | 3          | 3            | x       | x          | x    | x   | Metacarbonate |
| GRC-0430D  | M180161  | 1039.31   | 1          | 1            | x       | x          | x    | x   | Carbonaceous limey mudstone |

Methodology

Micro-XRF fundamental parameters standardless quantification

There are two general types of quantification methods for use with X-ray fluorescence spectra: standard-based (empirical) and standardless quantification procedures (such as fundamental parameters). Current methods for quantification of elemental abundances from XRF data use a fundamental parameters (FP) approach adapted from the Sherman equation (Sherman, 1955) to calculate concentrations from peak intensities (Thomsen, 2007; Flude et al., 2017). These methods are referred to as fundamental parameters methods, a name that comes from the set of parameters which describe X-ray interactions with atoms that are used to predict chemical proportions from X-ray peak intensities (Elam et al., 2004).

Micro-XRF data are collected from whole-rock samples rather than powders, producing two-dimensional arrays (maps) of XRF spectra that capture the spatial variation of elemental composition and mineralogy. Standardless FP quantification is considered to be the best option for quantification of μXRF data due to the large compositional variations found within small areas of most rock samples, which would otherwise require that a large set of reference materials be used in a standard-based quantification method (Kanngießer, 2003; Flude et al., 2017). This is further complicated by the potential difficulty in selecting a suitable reference material, which is homogeneous at the spatial scale of the μXRF beam (~20–100 μm). Given that the results of FP quantification are comparable to the standard-based method (Wegrzynek et al., 1998; Tagle and Reinhardt, 2016; Flude et al., 2017), it is difficult to justify using a standard-based approach for μXRF analyses.

Comparison of geochemical results from a standard-based quantification method and FP quantification shows that there is general agreement between the two methods (Wegrzynek et al., 1998). In the case of complicated samples (complex matrix with a high number of low Z elements) the FP algorithm performed slightly better at quantification. In a report by Tagle and Reinhardt (2016), they show that the FP quantification method available in the Bruker M4 software (Bruker, 2018b) performs well at quantifying homogeneous stainless-steel certified standards. Flude et al. (2017), however, found that the accuracy of the M4 FP method was diminished in some heterogeneous silicate material, but could be greatly improved using a hybrid standard-based/FP method, where a standard is analyzed and a type calibration was used to correct the FP results.

Micro-XRF geochemical maps for this study were produced on a Bruker Tornado μXRF scanner (Bruker, 2018c).
using a 100-\(\mu\)m step size and 25-\(\mu\)m spot size with standard conditions of analyses at 10 ms/pixel, two frame counts, and 50-kV acceleration voltage at the AuTec Laboratory in Vancouver, Canada. Quantitative chemical results were derived using the Bruker M4 (Bruker, 2015b) QMap fundamental parameters standardless quantification tool (Tagle and Reinhardt, 2016). The Bruker FP algorithm iteratively solves a variation of the Sherman equation, while automatically correcting for detector pile up and escape peaks to produce chemical concentrations using X-ray peak intensities. The FP algorithm uses a database of atomic fundamental parameters for each element (Flude et al., 2017), such as that from Elam et al. (2002). The final product for this study was elemental abundance in weight percent for Al, As, Ca, Fe, K, Mg, Mn, P, S, Si, and Ti, which were normalized to 100\%, circumventing systematic geometric factor errors in calculating X-ray intensities (Elam et al., 2004).

Prior to quantification of study samples, the elemental compositions of test samples were quantified using various extraction methods offered in the Bruker M4 software. Quantification can be done on every pixel (1 \(\times\) 1), or a grid of 3 \(\times\) 3, 5 \(\times\) 5, or 9 \(\times\) 9 pixels. Quantifying in a grid acts to increase the X-ray counts for each quantified sample (grid of pixels), which decreases the spread of the dataset (Fig. 2). The tradeoff is a loss in detail in the \(\mu\)XRF image as multiple pixels are averaged together. For this study, a 3 \(\times\) 3 grid quantification (i.e., integrating spectra from 9 pixels) was selected to decrease the spread in data while maintaining sufficiently high spatial resolution to preserve textures and resolve fine-grained minerals in \(\mu\)XRF maps.

**AMICS \(\mu\)XRF mineral identification**

Bruker Advanced Mineral Identification and Characterization System (AMICS) is a software package for identification of mineralogy from Bruker M4 Tornado \(\mu\)XRF and SEM-EDS data. For mineral identification using \(\mu\)XRF datasets, full X-ray spectra are evaluated and compared to a library of known characteristic XRF spectra, using \(\chi^2\) fingerprinting for a best-match mineral classification. Mineral classification can be further refined using various clustering techniques and/or manual manipulation and evaluation of XRF spectral attributes (Bruker, pers. commun.). The final product is a dominant mineral-class map with one mineral-class label (single or specific mineral mixture) per pixel.

**Micro-XRF-derived mineralogy from linear programming**

The samples analyzed in this study are fine-grained sedimentary rocks where the average grain size is <5 \(\mu\)m. Therefore, many of the 100-\(\mu\)m \(\mu\)XRF sample points contain mineral mixtures. In order to predict mineral abundance, it is therefore necessary to estimate the mineral proportions within each pixel. Here we employ quantified \(\mu\)XRF results derived from the rock sample surface to predict and quantify mineral abundances using linear programming (LP), or linear optimization. Braun (1986) demonstrated that LP could be used to calculate mineral proportions of montmorillonite, quartz, and plagioclase from chemical data and X-ray diffraction (XRD) results. Linear programming is a mathematical method in which a series of variables are minimized or maximized in order to reach an optimal solution given specific input constraints. In this case, LP is used to optimize the mineral proportions by calculating the proportion that makes use of the most geochemistry (maximization) within the constraints of the mineral formulae. This method has been shown to accurately calculate mineralogy in such applications as predicting acid rock drainage from multielement geochemistry (Berry et al., 2015), quantifying mineral contents of Martian soils (Cavanagh and Bish, 2016), and quantifying mineralogy of bentonites using multielement data (Braun, 1986).

Linear programming was used to calculate mineral abundances using quantitative geochemical results of \(\mu\)XRF analyses, using the lpSolve interface to LpSolve v. 5.5 (Berkelaar, 2019) in the R statistical programming language (R Core Team, 2017). In this method, LP was used to maximize the mineral content (objective function) using the available geochemistry in the expression:

\[
\max \{ c^T x \mid Ax \leq b \land x \geq 0 \},
\]

where \(c^T x\) is the objective function and the inequalities \(Ax \leq b\) and \(x \geq 0\) are the constraints for the optimization of the objective function. For this study, constraints for optimization include mineral stoichiometry (formulae derived from electron probe microanalyzer (EPMA) analyses), minerals present (as determined by XRD, mineral liberation analyzer (MLA), and EPMA), with constraints of a minimum value of zero (i.e., no minerals present), and maximum value of 100 (i.e., a sample is made up of only one mineral). This method produces multiple mineral labels with an estimated mineral proportion within each \(\mu\)XRF pixel.

**External validation**

Each of the 29 core samples (~8 \(\times\) 25 cm) that had been \(\mu\)XRF scanned were subsequently split so that one half could be crushed for validation work using homogenized powders. Each powder was scanned using the Bruker Tornado under the same operating conditions as the \(\mu\)XRF images. These powders were then fused into glass disks for analysis using the ARL ADVANCED XPert PRO X-ray diffraction (XRD) on a Bruker S8 TIGER at the University of Waikato. Results of the XRD analysis were used to validate the \(\mu\)XRF results. Splits of the same powders were then used for quantitative powder X-ray diffraction (XQRD) analysis to quantify mineral abundances.

The second half of drill core samples were used for EPMA and MLA analyses. Microprobe EDS and WDS results and backscatter images were collected using the JXA-8530F Plus field emission electron microprobe (EPMA) at the University of Tasmania Electron Microscopy and X-ray Microanalysis Facility. An FEI MLA 650 ESEM at the same facility was used for finer scale mineral identification and mapping of three subsamples of \(\mu\)XRF-scanned rocks. Reduced major axis (RMA) regression was used for independent variable comparisons (\(\mu\)XRF to WDS-\(\mu\)XRF, whole-rock geochemistry to \(\mu\)XRF, and LP results to XQRD) due to the associated error of each variable and the assumption of symmetry between them (see Smith, 2009, for full description of RMA). WDS-\(\mu\)XRF and whole-rock geochemical data were used to test the accuracy of the Bruker M4 \(\mu\)XRF FP data quantification method. The FEI MLA 650 ESEM was used to validate the qualitative mineral identifications from the \(\mu\)XRF images.
samples. XRD was used to identify minerals present for the LP algorithm and QXRD was used to assess the accuracy of the LP-derived mineral proportions.

Quantitative X-ray diffraction

Quantitative X-ray diffraction work was completed at the University of Alberta in the Environmental Economic Geology Laboratory. XRD data were collected in the Earth and Atmospheric Sciences XRD Laboratory. A 2- to 3-g split from each of 18 powders scanned by μXRF and WDS-XRF was ground under anhydrous ethanol with an McCrone micronizing mill for seven minutes, using agate grinding elements. Micronized samples were subsequently dried overnight then disaggregated and homogenized using an agate mortar and pestle.

A Ca exchange was performed on two samples that appeared to contain smectites (one contained smectite, the other interstratified illite-smectite). This was done using the method described by Mervine et al. (2018) in order to...
stabilize the basal spacing of smectites to 15 Å, following the advice of Bish et al. (2003). It also assisted with distinguishing between smectite and illite-smectite. These two samples were suspended in 100 mL of 1 M CaCl₂×2H₂O (Fisher Chemical, Certified ACS grade), sealed in Schott bottles, and agitated vigorously overnight using an orbital shaker. Following agitation, samples were gravity filtered through filter paper (Whatman no. 1). Samples were rinsed 3× with deionized water. They were then dried overnight at room temperature and disaggregated with an agate mortar and pestle.

Powder XRD patterns were collected from front-loaded samples using a Rigaku Ultima IV θ-θ powder X-ray diffractometer equipped with a D/Tex Ultra detector and a cobalt source that was operated at 38 kV and 38 mA. XRD patterns were collected from 5°–80° 2θ using a step size of 0.02° 2θ at a rate of 2° 2θ/min. For the two samples containing smectite or illite-smectite, relative humidity was recorded before and after each pattern was collected and a humidifier was run during sample analysis to maintain relative humidity in the range of 20 to 80% (after Bish et al., 2003).

Qualitative phase identification was conducted using the DIFFRAC.EVA XRD phase analysis software (Bruker) with reference to the International Center for Diffraction Data Powder Diffraction File 4+ database (ICDD PDF4+). Rietveld refinement (Rietveld, 1969; Hill and Howard, 1987; Bish and Howard, 1988) with XRD data was done to estimate mineral abundances using TOPAS 5 (Bruker). The fundamental parameters peak fitting protocol of Chevary and Coelho (1992) was used for all phases. Three samples produced patterns with significant anisotropic peak broadening in either calcite or dolomite; in the one instance that involved calcite, the model of Stephens (1999) was used to account for this effect, in the other two, a far better fit was obtained using two compositionally distinct structures for dolomite (i.e., one “high Ca,” one “low Ca”). The partial or no known crystal structure (PONKCS; Scarlett and Madsen, 2006) method of structureless fitting was used to model the peak profiles of kaolinite (where present at approx ≥10 wt %) and montmorillonite (wherever present) to account for turbostratic stacking disorder. The use of Rietveld-compatible structureless fitting methods, such as PONKCS, can result in overestimates of the structurally disordered phases for which they are used, owing to overestimation of peak intensities at the expense of other phases with overlapping peaks (Wilson et al., 2006; Turvey et al., 2018). This effect is particularly notable at low abundances; as such, where kaolinite was present at <10 wt %, the standard Rietveld approach for phase quantification (Hill and Howard, 1987; Bish and Howard, 1988) was used instead.

Elemental abundances were forward calculated from QXRD modal mineralogy using mineral formulae determined with EPMA results. The QXRD-derived chemistry was subsequently compared to whole rock XRF data for validation of QXRD results. As this study is focused on identifying typical Carlin-type mineral assemblages, metamorphic minerals and low abundance (<1%) phases identified using XRD data, such as actinolite, phlogopite, anorthite, siderite, hematite, anatase, and smectite, were not included in the µXRF maps presented; however, they were used to calculate elemental abundances for validation of QXRD results by comparison with XRF results.

### Results

#### Micro-XRF geochemical images and interpretation

Micro-XRF geochemical images show the relative variations of chemistry in a rock sample which, in turn, reflect the variations in mineralogy. For example, Figure 3A shows the µXRF-derived relative concentrations of Ca, Mg, and Mn of sample M180050, which are interpreted to reflect the presence and compositions of the carbonate minerals, dolomite and calcite, of this hydrothermally silicified limy mudstone. The sample has a complex network of crosscutting carbonate veins that appear to be syn- and postdecalcification. A comparison of the three-element µXRF image (Fig. 3A) to the true-color image (Fig. 3B) of the same sample illustrates that the hand sample has no visible indication of the variation of carbonate mineral chemistry within the veins. EPMA analyses and EPMA backscatter electron (BSE) images (Fig. 3C, D) confirm the presence of dolomite, Mg-Mn-calcite, and calcite in this sample, consistent with the µXRF image.

Figure 4 shows sample M180095, a limy mudstone sample with pervasive hydrothermal argilization and minor sulfidation and silicification. This sample reveals the relationship between µXRF-derived relative concentrations of K (cyan) and Al (red) (Fig. 4A), which is interpreted to reflect K-bearing (illite, and K-feldspar) and non-K-bearing aluminosilicates (e.g., kaolinite). Differences in the color, and its intensity, within grains and veins in Figure 4A and B reflect the variable K/Al ratio of these minerals. Thus, bright cyan represents the highest K/Al ratio (K-feldspar), light cyan to white shows a lower K/Al ratio (illite) and red shows the absence of K (kaolinite). In Figure 4A, K-feldspar is found primarily within breccia clasts, illite can be seen along fractures and in the breccia matrix, and kaolinite is primarily confined within the lower right corner of the image. In Figure 4B, kaolinite is concentrated preferentially along bedding planes and fractures that crosscut illite and K-feldspar. Potassium feldspar, illite, and kaolinite were also identified in the same sample using an MLA mineral map (Fig. 4C) and EPMA (EDS and EPMA-BSE imaging; Fig. 4D).

#### Micro-XRF fundamental parameters standardless quantification

In order to assess the accuracy of the fundamental parameters method, quantified µXRF results for major rock-forming elements (Al, Ca, Fe, K, Mg, and Si) were compared to the results of calibrated WDS-XRF analyses on glass disks created from the same powdered samples (Fig. 5). The R² values of 0.98 to 0.97 and intercepts near 0 suggest that the standardless FP method provides precise quantitative chemical results that can be used to estimate the abundance of mineral phases. The results of the RMA line for each element was used to correct the µXRF FP results for subsequent LP mineral calculations.

#### AMICS µXRF mineral identification

Figure 6 shows AMICS software results for mineral identification from the same sample seen in Figure 3 (sample M180050). This is a dominant mineral map where each pixel is labeled with a single mineral class (representing one or more minerals). The mineral map in Figure 6 highlights key mineral assemblages such as that associated with the host rock (calcite-illite-dolomite-quartz), silicification and
decalcification (quartz and calcite-quartz), chlorite alteration of the host rock (illite-chlorite-calcite-quartz), and hydrothermal veins (calcite, pyrite, Fe dolomite, Mn calcite).

A breakdown of mineral assemblages, along with the XRF spectral signature that represents each assemblage in AMICS for the hydrothermally altered sample M180080, also shown in Figures 3 and 6, illustrates that the mineral assemblage XRF photon energies of principal Kα X-ray lines (keV) are mostly consistent with the elemental signatures of the minerals identified (Willis et al., 2011). There are, however, some X-ray peaks that are unaccounted for in mineral classes such as pyrite, where the detection of Si and Ca suggests that there is contamination of the representative pyrite spectra with the chemical elements that make up surrounding matrix minerals.

**Linear programming (LP) μXRF mineral identification and quantification**

The LP approach to mineral quantification allows the abundance of each mineral in each μXRF pixel to be estimated, as opposed to the AMICS approach where pixels are given either single mineral or mineral mixture labels. The following results of the quantitative LP mineralogy estimates are from hydrothermally altered μXRF core samples. The LP mineral results were qualitatively validated using MLA and EPMA-BSE images from the same samples.

Figure 8 is a breakdown of the results of LP-derived mineralogy for sample M180080, which is also shown in Figures 3, 6, and 7. The results show that the LP method can be used to quantify calcite, dolomite, illite, pyrite, and quartz and that the textures in each mineral map are consistent with that of hydrothermally altered rock from Carlin-type gold deposits (Cline et al., 2005; Cline, 2018), revealing alteration textures such as silica replacement of calcite (silicification and decalcification, Fig. 8A, E) and the presence of carbonate veins (Fig. 8A, B). When coupled with the quantitative chemical data, the calcite veins were subdivided into Mn calcite, Mg calcite, and Fe calcite (Fig. 8F).

An LP-derived illite, calcite, and quartz composite image of a silicified carbonaceous limey mudstone breccia sample shows that calcite occurs within the limestone host rock and veins, and lower calcite abundances are consistent with decalcification within and adjacent to the breccia (Fig. 9A). Illite is disseminated in the sedimentary rock of the sample and is enriched along the contact between a breccia and siltstone.
Quartz abundance in this mineral map is interpreted to reflect hydrothermal silicification, as well as diagenetic quartz grains in the sedimentary rock. Similar mineralogical results are seen in the MLA image of the same sample (Fig. 9B); however, the MLA map contains a single label per pixel rather than multiple labels with mineral abundance.

A transect of quartz concentration from sample M180080 shows the location of silicification, as well as the gradational decrease in quartz moving away from the breccia into the adjacent rock (Fig. 9C). Overall, these images reveal in detail similar mineralogy and rock textures (e.g., decalcification and silicification) to those described for Carlin-type hydrothermal gold deposits elsewhere in Nevada (Emsbo et al., 2003; Cline et al., 2005; Vaughan et al., 2016).

The distribution of potassium feldspar and kaolinite were also calculated using LP (Fig. 10A). Figure 10A shows an LP-derived mineral map of illite, kaolinite, and K-feldspar as predicted from µXRF data. The LP results are consistent with the mineral textures identified in the MLA (Fig. 10B), and EPMA-BSE (Fig. 10C), which consists of fine-grained intermix of these three mineral phases. Electron probe microanalyses (Fig. 10D-F) confirm the presence of these minerals. This sample contains a silicification front with kaolinite disseminated throughout the sample, with illite and K-feldspar mostly confined to the unsilicified portion.

Validation of quantitative mineralogy derived from linear programming

Carbon concentrations were predicted from µXRF LP-derived mineralogy results (note that C is not measured by the µXRF instrument used in this study) and were compared to total carbon results from whole-rock geochemical analyses of the split core samples (Fig. 11). While this approach does not consider any potential organic carbon contribution to total C in the whole-rock samples, the concentration of carbonate minerals is likely much greater than organic C and thus organic carbon likely has a relatively minor impact on the results of this comparison. The high RMA $R^2$ value of 0.87, the slope of the RMA line near one ($m = 1.11$), and the intercept near zero ($b = -1.1$) shows that the LP prediction for carbonate...
(calcite and dolomite) mineral abundances are accurate for most samples, which suggests that the organic C assumption is reasonable. An outlier in Figure 11 has been overestimated in the mineral model compared to whole-rock LECO analysis. This may be due to a higher than normal contribution to Ca from minerals not included in the LP calculations, such as wollastonite, and not likely due to the presence of organic C due to the lack of organic C in this metacarbonates sample. The Ca in wollastonite of the outlier sample would cause an overestimate of C because Ca is assumed to be primarily within carbonate minerals.

Quantitative XRD (QXRD) was completed on selected µXRF samples for the purpose of validating µXRF-derived LP mineralogy results. Weighted pattern residual values, Rwp, for Rietveld refinements ranged from 1.9 to 6.0%, indicating good model fits to the observed data. It is important to note that the absolute and relative error on mineral abundances, as estimated from Rietveld refinement results, is typically greater at lower mineral abundances (e.g., Wilson et al., 2006, 2009). RMSE for chemical compositions calculated using QXRD results compared to quantified whole-rock µXRF results range from 0.42 (S) to 6.94% (SiO₂) (Table 3). The moderate to high correlation coefficient (R²) and regression line near y = x show that QXRD and µXRF analyses agree. Finally, mineral abundances predicted from µXRF data using the LP method are consistent with QXRD results, shown by high R² (0.82–0.97) and regression lines (QXRD vs. LP) near y = x (Fig. 12). Using QXRD as a baseline for comparison, RMSE for LP-derived mineralogy ranges from 0.91 (pyrite) to 7.15% (dolomite).

**Discussion: Micro-XRF Geochemistry Results and Interpretation**

The strength of the µXRF chemical mapping technique is in its ability to scan large core samples relatively quickly to reveal geochemical textures in rock samples that cannot be seen with the unaided eye (Ryan et al., 2018). An example is seen in Figure 3A and B that shows a µXRF chemical map for Ca, Mg, and Mn of a hydrothermally altered rock sample next to a true-color image of the same sample. The µXRF image shows many variations in the elemental composition of carbonate veins and host-rock carbonate that are not obvious in the true-color image. This may be of use in exploration when the carbonate vein composition can provide vectors toward mineralization such as that of the Mn calcite vein shown to
be associated with mineralization in a Carlin-type deposit in the Yukon (Steiner and Hickey, 2019). Micro-XRF composite chemical maps can also reflect specific mineralogy such as that of the K-Al maps that are interpreted to show illite, K-feldspar, and kaolinite (Fig. 4). Because of the fine scale of the μXRF beam, and the scale (~50 cm) over which that beam can be rastered, fine-scale mineralogical variations can be evaluated on a relatively large scale across a rock sample compared to what can be achieved using thin-section and SEM techniques. Thus, significantly more chemical and

![Fig. 5. Abundances of individual elements Al, Ca, Fe, K, Mg, and Si obtained from μXRF analyses compared to those obtained via WDS-XRF in atomic percent. Dashed line represents the RMA regression line between measured values. Thin gray lines represent the 95% confidence intervals. The thin black line shows the 1/1 line. Linear equation and R² value inset for RMA line.](image)

![Fig. 6. Mineral map derived from μXRF, using Bruker AMICS mineral identification software for sample M180080, a limey mudstone with hydrothermal silicification.](image)
Fig. 7. Breakdown of mineral classes (shown as black dots where present in samples) accompanied by XRF spectral signature as identified by the Bruker AMICS mineral identification software for sample M180080. Compare results to Figures 3A-D and 6. Percentage values shown for each mineral class are the area percent of each class identified in this sample.
Fig. 8. A.–E. Breakdown of LP-derived quantitative mineralogy results of μXRF sample M180080 seen in Figures 3A–D, 6, and 7. Each mineral map shows absolute mineral proportions. Abundance scale applies to (A–E). F. Geochemical maps of pixels identified to have more than 50% calcite that show three variations of calcite veins, Mn calcite (blue), Mg calcite (green), and Fe calcite (red).
textural information can be gleaned for the purpose of identifying associations of ore and alteration minerals. In addition, µXRF scanners allow more representative selection of rock samples or drill core and make sampling bias less likely due to the larger sampling volumes compared to other analytical methods such as SEM or EPMA.

**Conclusion: Comparison of AMICS and Linear Programming for Mineral Identification**

In fine-grained samples, the AMICS software identifies mineral groups (mixtures), such as those related to lithology (calcite-illite-quartz), hydrothermal alteration of the host rock (calcite-illite-dolomite-quartz, and calcite-quartz), and those pixels that fall along grain boundaries (calcite-illite-pyrite). If the grain sizes are larger than the pixel size, or there are large enough numbers of fine-grained minerals in a spatial cluster, the mineral class will be of a single mineral (calcite, pyrite, quartz, Fe dolomite, and Mn calcite). However, even those mineral classes that were identified as a single mineral (i.e., pyrite) have photon energy peaks from additional elements (e.g., Ca and Si). As there is no way to classify the vast number of possible mixture variations when three or four minerals may be mixed together, mineral mixtures for fine-grained samples cannot be accurately quantified using the AMICS method. In this case, the LP method offers significant advantages in that it can be used to quantify mineral mixtures. The LP method produces multiple mineral labels and abundances for each pixel, whereas AMICS provides a single label per pixel.

A potential drawback to calculating mineralogy using LP can be seen in the lower correlation coefficients of illite and K-feldspar predictions compared to QXRD results from the same samples. Because the chemical compositions of illite and K-feldspar are similar, when both minerals are present in a sample, especially in the presence of quartz and kaolinite, it is difficult to distinguish variations in the abundance of these phases. Potentially these results can be improved if the LP method was coupled with other mineral identification methods, such as LWIR or SWIR spectroscopy and/or qSEM.

The approach outlined here demonstrates that µXRF maps can be used to determine mineralogy, mineral abundances, and mineralogical textures not visible with the naked eye from...
fine-grained sedimentary rocks associated with Carlin-type Au deposits. This approach is transferrable to any ore deposit, but particularly sedimentary-hosted ore deposits where ore and gangue minerals are commonly fine grained and difficult to distinguish in hand specimen. Ultimately, improving our ability to map and predict the distribution of minerals within ore deposits is beneficial for improving our understanding of deposit genesis, recognizing the distribution of ore minerals and associations of ore and gangue minerals, as well as understanding and predicting how mineralogy may influence ore processing.

Fig. 10. A. Micro-XRF ($\mu$XRF)-derived (LP) mineral map of sample M180130 with illite (blue), kaolinite (green), and K-feldspar (red). White line drawn to show contact between silicification and host rock. White dots show the estimated location of the MLA and BSE images relative to the $\mu$XRF. B. MLA mineral map of the same sample, which shows mineralogy consistent with that identified with the LP method. C. EPMA-BSE image with EMPA points (red) that reflect similar mineralogy. D.-F. EPMA-EDS data for the three points from (C).

Fig. 11. Carbon from LECO analysis vs. carbon calculated from carbonate results of $\mu$XRF-derived linear programming mineralogy. Dashed line represents the RMA regression line between measured values. Thin gray lines represent the 95% confidence intervals. The thin black line shows the 1/1 line.
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Fig. 12. QXRD results compared to LP results for quartz, K-feldspar, pyrite, kaolinite, calcite, dolomite, and illite. R², slope, and intercept values of RMA regression line shown in each plot. Points from µXRF samples of this study that were analyzed using QXRD are highlighted for each plot for reference to the µXRF, MLA, and BSE figures.
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