Evaluating the Utility of Principal Component Analysis on EDS X-Ray Maps to Determine Bulk Mineralogy

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Due to advances in EDS technology, electron microscopy techniques have become an important tool to determine the relative abundance of mineral phases. However, few studies have directly compared EDS X-ray mineralogy with traditional techniques for assessing bulk mineralogy and elemental composition. We show that analysing a limited area (~0.5–3.2 mm²) of fine-grained metal extraction samples using EDS X-ray principal component analysis phase mapping yields results that agree within 10% with more traditional techniques for mineral phases present at greater than 5% m/m. Electron beam sensitive minerals, such as the carbonates, have poor correlations between EDS and X-ray Diffraction (XRD) and/or WD-XRF. Likewise, poor correlations between methods can be expected for particles that are smaller than the interaction volume of the electron beam (~1.5 µm); this strongly affected the phyllosilicates. One strength of EDS phase mapping is that it can identify phases present below the detection limit of powder XRD (<1%). Our results demonstrate that EDS phase mapping is sufficient to estimate bulk sample mineralogy. If polished thin sections have been prepared, this approach may save time and/or money relative to the more traditional approaches of preparing separate subsamples for XRD and/or WD-XRF.

Keywords: mineralogy, FEG-SEM, EDS, principal component analysis, XRD, WD-XRF, phase mapping.

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The limitations of automated EDS quantification routines have been well documented (Newbury and Bright 2005, Newbury 2009, Newbury and Ritchie 2013a). For automated EDS peak identification, X-ray energy spectral overlaps can be challenging to resolve. For example, the differences in energy between the S Ka (2.309 keV), Mo Lα (2.292 keV) and Pb Mα (2.342 keV) X-ray spectral lines are smaller than the ~ 120 eV resolution of a typical modern EDS detector. Therefore, the signal contributed by each element must be determined by peak deconvolution in post-processing rather than by the detector itself (Goldstein et al. 2018). Inadequate counting statistics (Newbury 2009) and lower beam energies (Newbury 2007) can lead to false or absent identification due to lack of counts at critical characteristic X-ray family peaks, especially for elements present at mass fractions near the detection limit (~ 0.1% m/m) (Newbury and Ritchie 2013b). ‘Standardless’ analysis quantification approaches can lack sufficient accuracy to determine a compound’s chemical formula (Newbury and Ritchie 2013b), and can fail entirely to identify trace elements (Newbury and Bright 2005). It is also important to have a grasp on the physical feasibility of the presence of a given element (Newbury and Bright 2005). A notorious example is the work of Mulligan et al. (1988) identifying physically improbable Tc in piscine calcium carbonate bony structures using EDS. Artefacts of the EDS method itself on the spectrum include sum peaks and silicon escape peaks. Modern software packages often remove these peaks, but the algorithms are proprietary (Goldstein et al. 2018). These limitations are inherent in the EDS technique and exist despite advances in instrumentation and software.

With spatially resolved mapping, there is the added challenge of accounting for the electron beam interaction volume in the sample, as well as the X-ray absorption of the sample, and how it affects the mapping output. These challenges are present in all X-ray microanalysis techniques, not just EDS. When an electron beam impinges on a sample, the beam spreads out in the sample into an interaction volume that is a function of the beam energy and the sample composition. Lower mean atomic number (Z) materials exhibit an increased scattering volume due to the decrease in elastic scattering cross section of the less massive atomic nuclei. The effect of the interaction volume is more complicated at phase boundaries and for small particles. Measuring on a phase boundary, phases with lower Z have a larger electron interaction volume and thus have a larger contribution to the mixed phase spectrum of the measured phase boundary than the phase with higher Z (Johnson et al. 2015). For small grains embedded in epoxy, which has low X-ray absorption, grains with lower Z will be detected as larger than same size higher Z minerals. Similar effects occur when analysing small particles as X-rays of different energies will be emitted differently from the sample based on the beam-sample-detector geometry. Spectral peak heights can vary based on the orientation of the detector relative to the particle as X-ray production is decreased compared with a bulk sample where the electron beam penetrates the edges of the sample (Kotula et al. 2003). The degree of X-ray absorption is highly dependent on mean Z of the particle (Goldstein et al. 2018).

The interaction volume of the electron beam impinging on different substrates can be simulated via Monte Carlo methods using CASINO v2.48 Monte Carlo simulation software (Drouin et al. 2007). Figure 1 shows a Monte Carlo simulation of the beam interaction volume when a 20 kV beam impinges on a boundary between quartz (SiO₂) and pyrite (FeS₂) grains. This shows the different sizes and shapes in the electron interaction volumes within each material, due to the differences in mean atomic number (Z) of the two minerals. The interaction volume in the quartz on the right is larger and more pear shaped, while the interaction volume in the pyrite on the left is smaller and more rounded. Although interaction volume is phase dependent, in most samples a 20 kV electron beam has an effective interaction volume of about 1–2 μm³. This interaction volume limits the spatial resolution of the phase identification and creates a spectral overprint near grain boundaries, resulting in spectrally unique artefact phases. For example, a several μm wide region adjacent to a K-feldspar-pyrite grain boundary, would generate a spectrum consisting of Fe, S, K, Al, Si and O. This is a mathematically unique phase, but does not represent a physical mineral phase, and the mineral assignment would need to be split.

Approaches for handling EDS data

Multiple EDS manufacturers offer versions of automated mapping hardware and software packages with different approaches to collecting and handling very large data sets. Popular approaches fall into either collecting EDS spectra and classifying minerals via matching with known data or purely mathematical approaches. Each approach has strengths and limitations.

Mineral-matching classification products such as QEMSCAN/MLA (FEI Inc., Hillsboro, OR, USA) (Reid et al. 1984, Gu 2003), TIMA (TESCAN, Brno, Czech Republic) (Hrstka et al. 2018), Mineralogic Mining (Carl Zeiss Microscopy GmbH, Jena, Germany) and INCAmineral (Oxford Instruments plc, Abingdon, UK) are optimised for high throughput. To facilitate this high sample throughput, they are typically configured with multiple EDS detectors and can be
configured to only collect data for particles or selected regions rather than a single field of view. They identify minerals based on combinations of backscattered electron (BSE) brightness and EDS spectral data, and find the most similar spectra in a lookup table obtained with identical operating conditions. Mineral identification with these tools is only as good as the lookup table; new phases can be misidentified, and unmatched spectra will be categorised as ‘unidentified,’ which the user may then investigate further. Additionally, they may incorrectly identify minerals with spectral overlaps, and fail to correctly identify minerals with extensive solid solutions (Johnson et al. 2015).

The primary advantage of using a stand-alone mathematical approach requiring no previous data inputs or spectra libraries, is that it does not rely on peak or elemental identification as a precursor to mineral phase identification and requires no a priori knowledge of the samples. Therefore, some of the challenges inherent to mineral-matching schemes can be overcome. For example, by looking at the entire spectrum rather than just specific X-ray lines, one is no longer reliant on correct peak identification and the confounding effects of peak overlaps are mitigated. Mathematical tools for handling the EDS data include derived spectra tools developed by Newbury and Bright (2005); elemental grouping approaches (van Hoek et al. 2016); and multivariate tools including principal components analysis (Kotula et al. 2003), clustering and neural networks as described by Bonnet (1998). Such mathematical tools segment the sample into phases, which the user identifies as minerals, based on the spectra of each unique phase found. Although the mathematical approach has advantages, it is not a panacea. This is a computationally intensive approach, and assigning a mineral to a unique spectral phase still relies on user expertise.

There are few studies comparing the representativeness of EDS mapping and phase identification with other analytical techniques. Goodall and Scales (2007), in their overview of analytical methods for characterising gold ores, compared automated mineralogy techniques with other microbeam methods (EPMA, Mössbauer spectroscopy, synchrotron XRF, TEM, LA-ICP-MS, SIMS, and PIXE methods) and emphasised the problem of representative sampling that limits every analytical technique. They also emphasised the inadequacy of characterising any ore sample with only a single analytical technique. Johnson et al. (2015) compared FEG-EPMA EDS and WDS X-ray mapping data sets processed with statistical techniques to QEMSCAN bulk phase mapping of the same analytical areas. They found the results from different techniques to be fundamentally similar, but with differences in the reported mineralogy and the
imaging quality. They concluded that the different results were primarily due to the different operating conditions of the two techniques and differences in the instrument features.

Studies using an element grouping approach to identify phases from EDS mapping data have shown broad general agreement with bulk analysis techniques. Van Hoek et al. (2016) compared two regions of EDS mapping deconvolved via an elemental grouping approach with bulk XRD on steel-making slag. They found discrepancies between the methods could be explained by mineral intergrowths and differences between the chemical and crystallographic definitions of a mineral phase. Alom et al. (2019) used this same elemental grouping approach to characterise the mineralogy of incinerator bottom ash by acquiring EDS maps of entire thin sections, as well as measuring bulk mineralogy via XRD and measured elemental mass fractions of fused bead WD-XRF. Discrepancies between their EDS results and XRD were attributed to large quantities of small particle sizes of the sulfates below the pixel size resolution of EDS, the presence of amorphous phases not determined by XRD, and the inability of EDS to determine the oxidation state of Fe oxide phases. Their bulk chemical compositions derived from EDS and XRF data generally agreed. Differences in the SiO2 and Fe2O3 results were attributed to a nugget effect where measured values were shifted from the true values due to non-uniform distributions of large particles enriched in SiO2 and/or Fe2O3 in the EDS data.

This study

The goal of this study is to evaluate the efficacy of using principal component analysis (PCA) (method of Kotula et al. (2003) on FEG-EDS X-ray mapping data sets collected on small regions of a grain mount totalling 0.51–3.2 mm² total area per sample, to determine the bulk mineralogy of ore processing samples. We chose ore processing samples as they are among the more complex types of samples in terms of grain size variation and mineralogy. By treating the data purely as a mathematical construct, choosing a spatially simple approach (Keenan and Kotula 2005), and applying a factor rotation to derive physically realistic factors (Keenan 2009), distinct mineral phases can be identified with spectra representing real compositions with no a priori knowledge of the samples. The Kotula et al. (2003) algorithm is commercially available as the Thermo Scientific Noran System 7 (NSS) EDS COMPASS phase mapping algorithm (Thermo Fisher Scientific, Waltham, MA, USA) (Kotula et al. 2003, 2007, Keenan and Kotula 2005). As of publication, the COMPASS algorithm is available as the Mountaineer option in Thermo Scientific’s Pathfinder X-ray Microanalysis software (Thermo Fisher Scientific, Waltham, MA, USA).

The mathematics behind the phase deconvolution of EDS spectral data are sound; however, the same limitations of spectral overlaps and correct peak identification still exist when it comes to quantification and mineral identification. A given spectral peak must be correctly identified to link it to the correct mineral assignment. The original spectrum of the pixels associated with a given phase can also be used to quantify the composition of the phase using peak fitting (Newbury and Bright 2005).

Analysing a full thin section can consume large amounts of instrument time—on the order of tens of hours per thin section depending on the instrumental parameters selected. Here we compare the EDS mapped phases of a small portion of a gran mount (three fields of view ranging from 0.475 mm × 0.356 mm to 1.186 mm × 0.890 mm in size depending on the sample grain size and resulting magnification selected) with mineralogy determined by bulk methods – powder XRD for bulk mineralogy and WD-XRF for bulk composition. The purpose of this study is to identify strengths and limitations of using the COMPASS technique on subsamples of a fine-grained material in order to assess its potential for significant instrument time savings in determining bulk mineralogy.

Experimental procedure

Sample collection and preservation

Samples were collected from two gold extraction mills and one copper extraction mill in conjunction with mill staff. Samples with prefix GS were collected in July 2012 from Golden Sunlight (Whitehall, MT, USA); samples beginning with prefix PG were collected in May 2016 from Sumitomo Pogo (Delta Junction, AK, USA); samples beginning with prefix AS were collected in March 2012 from the ASARCO Mission Mine (Sahuarita, AZ, USA) and Hayden Operations (Hayden, AZ, USA). Samples from Golden Sunlight and Pogo were frozen within 24 h of collection and freeze-dried using a Labconco (Kansas City, MO, USA) FreeZone Freeze Dryer. ASARCO samples were received dry. Samples included ore at various stages of grinding–gravity concentrates and tailings; flotation feeds, tailings, and concentrates; copper concentrates; and cyanide tailings. We used a riffle splitter to obtain representative aliquots of each sample for analysis by EDS, WD-XRF, and XRD. All samples were stored in acid-washed plastic bottles at room temperature prior to being prepared for analysis.
Phase mapping with X-ray EDS

Billets were prepared by embedding samples in EPO-TEK 301-2FL epoxy (Epoxy Technology, Inc., Billerica, MA, USA) and curing under a vacuum for 3 days. We polished the billets using 1000 grit SiC on glass, followed by 3 \( \mu m \) alumina on glass. The final polish was with 0.05 \( \mu m \) alumina suspension on silk on glass. This polishing protocol helped to minimise over-polishing and plucking of the fine-grained samples. Billets were then carbon coated with an Edwards Coating System 306A (Edwards Vacuum, Burgess Hill, UK) to thickness of \( \sim 250 \) Å.

Grain scale mineralogy was determined using X-ray EDS, using a JEOL (Tokyo, Japan), JXA-8530F EPMA housed at the University of Alaska Fairbanks (UAF), Advanced Instrumentation Laboratory (AIL), outfitted with a Schottky-type field emission electron source and a Thermo Scientific UltraDry EDS (Thermo Fisher Scientific, Waltham, MA, USA). For most samples, we randomly selected three separate areas (approximately 20 mm apart) from each billet for phase mapping analysis using Thermo Scientific NSS v. 3.3 software (Thermo Fisher Scientific, Waltham, MA, USA). Total areas analysed per sample (Table 1) ranged from 0.51 to 3.17 mm\(^2\). We set the beam accelerating voltage to 20 kV to excite K-line X-rays of the transition metals and L lines from heavy metals. We adjusted the current to generate a detector dead time of \( \sim 40\% \), which is the optimum for this detector. Typically, this resulted in a beam current of \( \sim 280 \) nA. We chose the magnification based on the mean size of the grains in a given sample. Magnification setting on the EPMA ranged from \( \times 9100 \) to \( \times 9250 \), corresponding to 1.159 and 0.464 \( \mu m \) per pixel, respectively. Typical sample grain sizes and representative BSE images with scale bars are shown in Figure 2. For samples with abundant \( \sim 1-2 \) \( \mu m \) grains, we set the magnification to \( \times 250 \); for samples with larger particles, magnification between \( \times 250 \) and \( \times 100 \) was used. A 20 kV beam has a mean excitation volume of 1.5 \( \mu m^3 \) in these samples; higher energy X-rays will have a slightly smaller interaction volume, but in general increasing magnification beyond \( \times 250 \) does not generate improved X-ray map resolution. For the spectral imaging settings, the resolution was set to 1024 \( \times \) 768 pixels, with a dwell time per pixel of 127 \( \mu s \). A frame is an acquisition of an X-ray spectrum at each pixel of the analytical area with a given dwell time per pixel. We set the software to terminate the acquisition after 500 frames, or when the mean counts per pixel reached 100 counts, whichever came first. Typical measurement times were on the order of 15 min. This ensured sufficient counting statistics for the phase analysis (Kotula et al. 2003).

| X, Y Field of view (\( \mu m \)) | Field of view area/Sample area (mm\(^2\)) |
|---------------------------------|----------------------------------------|
| AS 346                         | 598                                    | 0.29                          |
|                                | 479                                    | 0.86                          |
| AS 352                         | 598                                    | 0.29                          |
|                                | 479                                    | 0.86                          |
| GS 403                         | 1187                                   | 1.06                          |
|                                | 890                                    | 3.17                          |
| GS 405                         | 1187                                   | 1.06                          |
|                                | 890                                    | 3.17                          |
| GS 406                         | 475                                    | 0.17                          |
|                                | 356                                    | 0.51                          |
| GS 407                         | 475                                    | 0.17                          |
|                                | 356                                    | 0.51                          |
| GS 409                         | 1187                                   | 1.06                          |
|                                | 890                                    | 3.17                          |
| GS 410                         | 1187                                   | 1.06                          |
|                                | 890                                    | 3.17                          |
| GS 411                         | 1187                                   | 1.06                          |
|                                | 890                                    | 3.17                          |
| GS 412                         | 1187                                   | 1.06                          |
|                                | 890                                    | 3.17                          |
| GS 413                         | 475                                    | 0.17                          |
|                                | 356                                    | 0.51                          |
| PG 601                         | 698                                    | 0.37                          |
|                                | 524                                    | 1.10                          |
| PG 603                         | 742                                    | 0.41                          |
|                                | 557                                    | 1.24                          |
| PG 604                         | 792                                    | 0.47                          |
|                                | 594                                    | 1.41                          |
| PG 606                         | 698                                    | 0.37                          |
|                                | 524                                    | 1.10                          |
| PG 607                         | 594                                    | 0.26                          |
|                                | 445                                    | 0.79                          |
| PG 608                         | 625                                    | 0.29                          |
|                                | 468                                    | 0.88                          |
| PG 609                         | 594                                    | 0.26                          |
|                                | 445                                    | 0.79                          |
| PG 610                         | 594                                    | 0.26                          |
|                                | 445                                    | 0.79                          |
| PG 612                         | 625                                    | 0.29                          |
|                                | 466                                    | 0.87                          |
| PG 621                         | 594                                    | 0.26                          |
|                                | 445                                    | 0.79                          |
| PG 622                         | 594                                    | 0.26                          |
|                                | 445                                    | 0.79                          |

The top value in a pair is the X dimension.

To perform the COMPASS phase extraction, we chose the ‘area method’. This produces a ‘spatially simple’ set of principal components with high spatial resolution. As most real samples will only contain a few components present in a given pixel, using a ‘spatially simple’ approach provides more physical insight into real samples than a ‘spectrally simple’ method (Keenan and Kotula 2005). We chose the...
internal model for the background and selected 120 eV low energy cut-off to eliminate low-frequency noise. We limited the number of components to thirteen to minimise the computation time necessary for the subsequent Xphase spatial segmentation option. Thirteen components took 10–15 min for the Xphase spatial segmentation extraction on the fastest computer at our disposal. Each additional component nearly doubles the phase extraction time. Both the Xphase and the ‘maximum intensity’ options for spatial segmentation produce similar spatial phase maps. However, only the Xphase extraction method produces a real spectrum that can be quantified (Suzuki and Camus 2020).

Figure 2. Backscattered electron (BSE) images of selected samples showing typical particle assemblages. Samples that were predominantly fine-grained were imaged and analysed at × 250 while samples with larger-sized particles were imaged at lower resolutions, down to × 100. Magnification refers to instrument settings; scale bars are present in the lower right of each image. BSE images materials with higher mean atomic number (Z) as brighter. White mineral grains are typically sulfides, medium grey grains are predominantly silicates, and black regions are the epoxy matrix. Brightness scales are not uniform across images due to slightly different analytical conditions necessary to optimise dead time for each sample.
We chose the minimum area for a phase to be 0.1% of the field of view as that was below the detection limits of the XRD data, and to determine how well the COMPASS routine could detect and identify minor phases. Minimum areas < 0.1% were too computationally intensive to be worthwhile for the computers at our disposal.

Figure 3. Phase map extraction. Phases were mathematically segmented via the software and minerals were manually identified based on “standardless” quantification data. A backscattered electron (BSE) image of the sample (GS403-1) with a scale bar is shown for reference.

Figure 4. ImageJ particle sizes. BSE Images had thresholds applied and were segmented in ImageJ to determine particle sizes. Particles for all three analytical regions per sample were combined.
Table 2.
Weight per cent mineralogical abundance from EDS phase mapping data with % relative standard deviation (% RSD)

|          | AS 346 |          | GS 403 |          | GS 405 |          | GS 406 |          | GS 407 |
|----------|--------|----------|--------|----------|--------|----------|--------|----------|--------|
|          | Mean % RSD | Mean % RSD | Mean % RSD | Mean % RSD | Mean % RSD | Mean % RSD | Mean % RSD | Mean % RSD | Mean % RSD |
| Quartz   | 3.9    | 22       | 0.81   | 71       | 4.5    | 10       | 6.7    | 3        | 6.0    | 65       | 5.1    | 42       |
| Albite   | 0.36   | 102      | 0.043  | 173      | 4.5    | 10       | 6.7    | 3        | 6.0    | 65       | 5.1    | 42       |
| Feldspar (Ca-rich) | 1.2  | 92       | -      | -        | -      | -        | -      | -        | -      | -        | -      | -        |
| K-feldspar | 1.6  | 38       | 1.1    | 23       | 32     | 4        | 33     | 7        | 32     | 21       | 26     | 16       |
| Clays    | -      | -        | 0.056  | 173      | 0.57   | 159      | -      | -        | 1.1    | 63       | -      |          |
| Chlorite | 0.82   | 142      | 0.47   | 173      | 2.3    | 89       | 3.0    | 1        | 0.39   | 75       | 3.1    | 38       |
| Biotite  | -      | -        | -      | -        | -      | -        | -      | -        | -      | -        | -      | -        |
| Muscovite | -   | -        | -      | -        | -      | -        | -      | -        | -      | -        | -      | -        |
| Zircon   | 0.33   | 146      | 0.48   | 99       | -      | -        | -      | -        | 0.56   | 88       | -      | -        |
| Silicates, other | -  | -        | -      | -        | -      | -        | -      | -        | 0.12   | 88       | -      | -        |
| Apatite  | -      | -        | -      | -        | -      | -        | -      | -        | -      | -        | -      | -        |
| Svanbergite | -  | -        | -      | -        | -      | -        | -      | -        | -      | -        | -      | -        |
| Monazite | -      | -        | -      | -        | -      | -        | -      | -        | -      | -        | -      | -        |
| Gypsum   | -      | -        | 0.075  | 173      | -      | -        | -      | -        | -      | -        | -      | -        |
| Barite   | -      | -        | -      | -        | 0.38   | 138      | 0.61   | 0        | 0.37   | 80       | 1.2    | 18       |
| Carbonates, other | 0.90 | 22       | 0.51   | 97       | 2.0    | 41       | 6.5    | 8        | 2.5    | 14       | 2.2    | 27       |
| Calcite  | -      | -        | -      | -        | 0.061  | 38       | -      | -        | 0.10   | 92       | 0.09   | 92       |
| Micaesite | -    | -        | -      | -        | 2.8    | 86       | 1.3    | 1        | 2.0    | 76       | 2.3    | 75       |
| Cassiterite | -  | -        | -      | -        | -      | -        | -      | -        | -      | -        | -      | -        |
| Rutile   | -      | -        | 0.065  | 173      | 0.79   | 17       | 0.34   | 0        | 0.90   | 55       | 0.88   | 52       |
| Al oxide | -      | -        | -      | -        | -      | -        | -      | -        | -      | -        | -      | -        |
| Fe oxide | -      | -        | 0.38   | 173      | 1.9    | 165      | 0.83   | 0        | 1.4    | 29       | 2.3    | 91       |
| Imitcrite | -    | -        | 0.25   | 173      | 2.2    | 141      | -      | -        | 0.58   | 149      | -      | -        |
| Chromite | -      | -        | -      | -        | -      | -        | -      | -        | -      | -        | -      | -        |
| Urolspinol | -  | -        | -      | -        | -      | -        | -      | -        | -      | -        | -      | -        |
| Perovskite | - | -        | -      | -        | -      | -        | -      | -        | -      | -        | -      | -        |
| Arsenopyrite | -  | -        | -      | -        | -      | -        | -      | -        | -      | -        | -      | -        |
| Loellingite | -  | -        | -      | -        | -      | -        | -      | -        | -      | -        | -      | -        |
| Pyrite   | 43     | 27       | 6.3    | 58       | 11     | 48       | 12     | 3        | 18     | 10       | 22     | 5        |
| Molybdenite | 1.1  | 31       | 2.1    | 97       | -      | -        | -      | -        | -      | -        | -      | -        |
| Ttntdymite | -    | -        | -      | -        | -      | -        | -      | -        | -      | -        | -      | -        |
| Chalcoprite | 44   | 12       | 85     | 20       | -      | -        | -      | -        | -      | -        | -      | -        |
| Sphalrite | 0.99  | 51       | 0.44   | 86       | -      | -        | -      | -        | -      | -        | -      | -        |
| Covellite | 2.9   | 59       | -      | -        | -      | -        | -      | -        | -      | -        | -      | -        |
| Fluorite | -      | -        | -      | -        | 0.77   | 1        | -      | -        | -      | -        | -      | -        |
| XYZ phase | -    | -        | -      | -        | -      | -        | -      | -        | -      | -        | -      | -        |

Each sample was analysed over three spatially distant regions. – indicates mineral not detected.
| GS 409 | GS 410 | GS 411 | GS 412 | GS 413 |
|--------|--------|--------|--------|--------|
| Mean   | % RSD  | Mean   | % RSD  | Mean   | % RSD  | Mean   | % RSD  | Mean   | % RSD  |
| 21     | 19     | 25     | 16     | 25     | 9      | 35     | 15     | 80     | 18     |
| 13     | 19     | 65     | 41     | 74     | 12     | 12     | 34     | 1.5    | 43     |
| 40     | 10     | 30     | 34     | 33     | 17     | 34     | 19     | 10     | 22     |
| 1.8    | 89     | 0.38   | 94     | 0.22   | 133    | 0.88   | 91     | 1.0    | 53     |
| 37     | 13     | 90     | 69     | 17     | 58     | 52     | 52     | 3.2    | 16     |
|        |        |        |        |        |        |        |        |        |        |
| 0.12   | 151    |        |        |        |        |        |        |        |        |
| 40     | 10     | 30     | 34     | 33     | 17     | 34     | 19     | 10     | 22     |
| 1.8    | 89     | 0.38   | 94     | 0.22   | 133    | 0.88   | 91     | 1.0    | 53     |
| 37     | 13     | 90     | 69     | 17     | 58     | 52     | 52     | 3.2    | 16     |

| PG 608 | PG 609 | PG 610 | PG 612 | PG 621 | PG 622 |
|--------|--------|--------|--------|--------|--------|
| Mean   | % RSD  | Mean   | % RSD  | Mean   | % RSD  | Mean   | % RSD  | Mean   | % RSD  | Mean   | % RSD  |
| 62     | 5      | 68     | 2      | 38     | 24     | 49     | 4      | 46     | 14     | 49     | 18     |
| 1.4    | 53     | 20     | 65     | 1.1    | 90     | 1.2    | 80     | 3.1    | 29     | 2.6    | 64     |
| 10     | 44     | 60     | 44     | 5.4    | 3      | 4.7    | 72     | 4.2    | 94     | 3.5    | 90     |
| 0.67   | 47     | 0.79   | 96     | 0.84   | 173    | 0.84   | 128    | 0.13   | 173    | 0.993  | 173    |
| 15     | 41     | 14     | 10     | 16     | 82     | 13     | 39     | 10     | 48     | 9.5    | 52     |
| 0.38   | 90     | 0.18   | 121    |        | 0.0011 | 173    | 0.16   | 112    | 0.16   | 173    |
|        |        |        |        |        |        |        |        |        |        |        |        |
| 0.05   | 173    |        |        |        |        |        |        |        |        |        |        |
| 4.05   | 4.2    | 2.2    | 10     | 0.87   | 57     | 0.71   | 112    | 0.16   | 173    |
| 0.59   | 173    | 0.49   | 173    | 1.6    | 173    |        | 0.55   | 173    | 3.2    | 89     |
|        |        |        |        |        |        |        |        |        |        |        |        |
| 0.08   | 173    | 0.14   | 173    | 0.59   | 173    |        |        |        |        |        |        |
| 1.8    | 55     |        |        | 1.3    | 21     | 0.19   | 173    |        |        |        |        |
| 1.05   | 173    |        |        |        |        |        |        |        |        |        |        |
| 0.12   | 173    |        |        |        |        |        |        |        |        |        |        |

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Mineral identification of a given unique phase statistically identified by the EDS was done manually by comparing the phase spectrum to EDS spectra compiled by Severin (2004). However, if a match was not obvious, we would try to find a homogenous region of the identified phase ~20–50 µm in size. We would then collect a spot analysis offline on the collected EDS data cube to generate a clean spectrum in that region. We would then use the software’s auto peak id function to identify peaks, correcting peak identification as necessary, and then run the “standardless” quantification algorithm, and check with linear least squares peak fitting (Newbury and Bright 2005). Fe oxide and Al oxide minerals were difficult to identify due to challenges in quantifying O and H via EDS. Phases with Fe and O present were assigned to Fe oxide, and likewise with Al. This approach is very sensitive to minor changes in composition as well as haloes of a mineral in the epoxy, subsurface grain haloes, or the region where minerals touched, all were identified as unique phases. These mixed phases were manually assigned to a phase based on BSE images, spot analyses, and spectral identification. Mineral names, formulae, and abbreviations are listed in Table S1. To minimise incorrect peak identifications during the mineral identification of phases, we omitted C (as the samples were carbon coated), Tc, Pd, Hg, and the REEs from the potential element list. To clarify, during the COMPASS phase extraction, all phases with Fe and O present were assigned to Fe oxide, and likewise with Al. This approach is very sensitive to minor changes in composition as well as haloes of a mineral in the epoxy, subsurface grain haloes, or the region where minerals touched, all were identified as unique phases. These mixed phases were manually assigned to a phase based on BSE images, spot analyses, and spectral identification. Mineral names, formulae, and abbreviations are listed in Table S1. To minimise incorrect peak identifications during the mineral identification of phases, we omitted C (as the samples were carbon coated), Tc, Pd, Hg, and the REEs from the potential element list. To clarify, during the COMPASS phase extraction, all spectral data are utilised to mathematically identify unique phases, it is only during the final manual step of mineral assignment to the COMPASS mathematically unique phase that these elements were omitted. The resulting COMPASS output with mineral phases and epoxy regions identified is shown in Figure 3.

Each analytical area was characterised for bulk particle size statistics independent of mineral phases and the COMPASS extraction. The particle size statistics were calculated using ImageJ (Schneider et al. 2012). Thresholds were applied to BSE images, and then the BioVoxxel watershed irregular features toolbox was used to segment the thresholded images (Brocher 2015). We then used the wire frame tool to outline individual particles (Figure 4). Particles < 1.5 µm² in area were rejected as this was the approximate excitation volume of the electron beam in the sample. Particle area statistics from the three analytical regions were combined, tabulated, and log transformed. Log transformed particle size distributions are plotted in Figure S1.

**Bulk mineralogy**

Bulk weight per cent mineral abundances were determined via powder XRD. Samples were micronised for 10 min in an XRD-Mill McCrone (McCrone Group, Westmont, IL, USA) using agate grinding elements (O’Connor and Chang 1986). Approximately 2 ml of sample and ~ 7 ml of 99% v/v isopropyl alcohol were added to each vial. After micronising, samples were rinsed out of the micronising vial using alcohol, dried, and sieved using a 40-mesh sieve. Samples were packed into 3 cm side loaded aluminium sample holders designed to mitigate preferential orientation effects (da Silva et al. 2011).

Mounted samples were analysed on a PANalytical (Almelo, The Netherlands) Xpert Pro Diffractometer (XRD) with an X'Celerator detector at the USGS Powder X-Ray Diffraction Laboratory, Reston, VA, USA (Piatok et al. 2014). A Cu Ka radiation source was used, scanning 3 to 80° 2θ at 0.017° 2θ step size for 60 s per step. We used PANalytical X'Pert HighScore Plus v4.5 software and reference structure data from the Crystallography Open Database (COD) 2013 (Grazulis et al. 2009) to identify and quantify minerals via Rietveld refinement (Rietveld 1969, O’Connor and Raven 1988). Our identification of minerals was informed by our EDS results. Rietveld refinement is a methodology that reconstructs the measured powder diffraction pattern based on structural parameters. These factors are refined using a least squares fitting method until the misfit between the theoretical profile and the measured profile is minimised. We refined the specimen displacement, scale factors, background, unit cells, peak profile fittings and asymmetry, and preferred orientation. Site occupancies and mineral chemistry were not refined. Rietveld analyses typically have mineral detection limits on the order of 1% m/m or better for crystalline phases present in the sample (León-Reina et al. 2016).

**Bulk chemical composition**

Bulk chemical composition analysis was performed by WD-XRF (Beckhoff et al. 2006). For WD-XRF analysis, subsamples were ground in a Spex (Metuchen, NJ, USA) 8000D Mixer/Mill in hardened steel vials (Spex Part # 8001). Quartz sand was ground in the vials for 3 min between samples. The vials were then rinsed in water and wiped down with 99% v/v isopropyl alcohol. Vials were loaded with approximately 12.5 g of sample, 1.25 g of PXR-225 binder (Premier Lab Supply, Port St. Lucie, FL, USA) and 7 ml of Vertrel XF grinding agent (Miller-Stephenson, Danbury, CT, USA) and ground for 4 min (Anzelmo et al. 2001). After the Vertrel XF evaporated in a fume hood, the sample was pressed into a 40 mm diameter pellet via a hydraulic bottle jack at 20000 psi for 2 min.

The pellets were analysed using a PANalytical (Almelo, The Netherlands) Axios four kilowatt WD-XRF spectrometer
housed at the UAF AIL. Samples were analysed with a modified version of PANalytical's Omnian routine. We modified the default Omnian routine by adding additional sulfide- and arsenic-rich reference materials to more closely match the matrix of our samples. Oxide and element mass fractions are tabulated in Table S3. Individual sample mineralogy was calculated based on the oxide and element mass fraction measurement results following the general procedure of a CIPW norm calculation, but with different minerals and elements. EDS and XRD results were used to constrain mineral assignments. Therefore, the XRF results are dependent on the other analytical method data sets. Mineral phases with a unique element (i.e., Mo in molybdenite) were calculated first, and the consumed non-unique elements (i.e., S in molybdenite) were subtracted off the element totals prior to beginning the next calculation. We used end-member mineral compositions unless EDS or XRD indicated another composition would be a better choice. Mineral formulae from Deer et al. (2013) and Anthony et al. (2019) were used and are included in Table S1. Minerals that shared multiple elements, such as muscovite and potassium feldspar, were calculated simultaneously to optimise assigning how much of the shared elements each mineral would consume.

Comparison of results

In order to compare not just the results per mineral between methods for each sample, but to compare results of each sample, we defined a goodness of agreement (GOA) metric and calculated it for each sample. This GOA metric compared the results of EDS and XRD, and EDS and WD-XRF analyses to help determine if certain types of samples were better characterised by the EDS COMPASS approach. We calculated the GOA metric by normalising EDS area phase abundances to 100% after removing the epoxy ‘phase’. The EDS area per cent abundances were converted to weight per cent abundances using the mineral densities (Delesse 1848). A 2D to 3D stereological transformation is not possible using only 2D data with complicated grain shapes, and this approach will be biased towards overestimating contributions from smaller grains (Jones 1987). EDS phases present at greater than 5% m/m were labelled as major phases. The relative per cent difference was calculated between each major EDS phase in a given sample and the amount determined by XRD and WD-XRF. These values were summed and the mean variance per sample was calculated based on the number of major phases present as measured by EDS yielding a GOA metric. The equations for calculating the GOA metrics are in Appendix S1. A low GOA score indicates greater agreement between analytical methods than a higher GOA score.

Bivariate statistical analysis using JMP 13.1.0 software (SAS Institute, Inc., Cary, NC, USA) was performed to elucidate the relationships between the EDS results and the XRD and WD-XRF results, respectively, as well as the GOA scores. Mineralogical abundance results between EDS and XRD, and EDS and WD-XRF were statistically compared for linear correlations using bivariate analysis. Bivariate analysis was performed for all samples, and for PG and GS sample subsets for EDS log-transformed particle statistics, EDS mineral phases, major oxide and element composition measured from WD-XRF, and mineral abundances determined by XRD.

Results

Phase mapping with X-ray EDS

EDS mineral phase abundances (Table 2) were broadly similar across the three analytical regions examined in each sample. The % RSD (per cent relative standard deviation) generally decreased with increasing mean weight per cent; for > 21% m/m the RSD is generally < 35% and means 13%. There is greater variation for lower abundance minerals than for higher abundance ones as shown in Figure 5a. Various minor phases were detected in each sample, but the same minor phases were not always detected in each analysis region for a given sample (Table 2). Even though we set the software for a minimum phase area threshold of 0.1% of the field of view, this is large in terms of particle size. This threshold would miss detecting a phase present that consisted of only a single grain with a radius of 18 µm for the samples magnified at x 100 and 7 µm for the samples magnified at x 250 (see representative BSE images in Figure 2). Phase area thresholds < 0.1% of the field of view were not computationally practical for the computers at our disposal. Identification of minor phases is often important for addressing scientific questions. Minor phases often exist below the detection limit of XRD and can help indicate which phases host minor elements detected by WD-XRF.

Comparison of techniques

EDS phase abundances were also broadly similar to mineral phase abundances obtained by XRD and WD-XRF as shown in Table 3. A comparison of the major phases (Figure 6) also indicates broad agreement between the techniques, with values measured typically within 10% of each other. Low concentration phases displayed a greater
The linear regressions between EDS and XRD, and EDS and WD-XRF for major phases reveal differences in offsets (y-intercept), the analytical agreement (slope) between the methods, as well as differences in coefficients of determination ($R^2$) for different phases (Figure 7). Most of the y-intercepts are close to zero, with offsets of a few per cent, with the exception of muscovite, which is close to ten per cent for both EDS-XRD and EDS-XRF. The carbonates and muscovite have very poor analytical agreement between EDS and XRF and XRD, respectively, with slopes of 0.6 or less. Quartz and K-feldspar have slopes greater than 0.93 indicating excellent agreement for those minerals between EDS and XRF and XRD. (Perfect agreement would be a slope of 1.) Pyrite has moderate agreement with an EDS-XRD slope of 0.88 and an EDS-XRF slope of 0.78. Albite and arsenopyrite have better agreement with XRD (slope > 0.96) than with XRF analysis (slopes ~ 0.5). Chlorite is the opposite, with better agreement via XRF (slope ~ 1.1) than with XRD (~ 0.6), but poor coefficients of correlation (~ 0.1). For quartz, albite, potassium feldspar, and pyrite, the coefficients of determination explained more than 70% of the variability between methods. This is consistent with their slopes being close to 1. For arsenopyrite, 69% and 41% of the variability were explained by the XRD and WD-XRF, respectively. The linear regression relationships explained almost none of the variability for chlorite, muscovite, calcite, and the other carbonates.

Sample parameters important to agreement

The GOAs for each sample are tabulated in Table 3. The GOA bivariate analysis results are tabulated in Table S7 for the EDS-XRD GOA and in Table S8 for the EDS-WD-XRF GOA. Correlation strengths greater than the absolute value of 0.5 (moderate correlations and stronger) are in bold. In general, the PG sample subset has more parameters correlated with the GOA metric than the GS samples. The GS samples have a moderate anti-correlation of the XRF GOA with the muscovite as measured by EDS, and a moderate anti-correlation of the XRD GOA and the median of the particle size distribution. For the PG sample subset, the XRF GOA is moderately anti-correlated with arsenopyrite measured by EDS, and moderately correlated with chlorite and K-feldspar via EDS, and Al$_2$O$_3$ and K$_2$O mass fractions by XRF.

Examining the XRD GOA for the PG samples, it is moderately anti-correlated to the mean of the particle area distribution, and to the amount of arsenopyrite determined by EDS. The XRD GOA is strongly correlated ( > 0.75) with the total number of particles, and moderately correlated with carbonates by EDS, pyrite by EDS, CaO and Na$_2$O mass fractions by XRF, and chlorite by XRD.
Discussion

Establishing sample modal mineralogy is frequently the first step of sample characterisation in geological studies. Powder XRD and WD-XRF are established techniques with widespread acceptance for sample characterisation. Powder XRD provides structural information yielding mineralogical identification, but has detection limits of ~1% m/m (Leon-Reina et al. 2016). WD-XRF measures composition with a high degree of precision and has detection limits < 10 µg g⁻¹, but provides no structural information to determine mineralogy. The EDS COMPASS approach, evaluated here, can provide relatively rapid-grain scale mineralogy. Each of these techniques can inform the other, but for real-world samples, such as those used in this study, there are no reference values for comparison. Our discussion will therefore be framed by comparing results of the newer technique (EDS COMPASS) to mismatches in results with the more established bulk characterisation techniques of XRD and WD-XRF.

There is broad agreement of the major phases determined by the EDS COMPASS approach, and XRD and WXRF as shown in Figure 6. Various minor phases were found in all samples by all methods (Tables S2, S4 and S5). The correlation and regression relationships used to investigate the difference in results between the EDS COMPASS approach and the XRD and WD-XRF approaches to mineralogy reveal that some minerals correspond better than others. Much of this variation can be explained by sample particle size, the characteristics of specific minerals, the interaction of individual grains with the electron beam, and fundamental differences in the analytical methods. Examining the roots of the disagreement between these techniques can help reveal when the PCA approach on limited sample areas to EDS mineral abundance is likely to work best and when caution is warranted.

Interaction of the electron beam

The intersection of the beam interaction volume with grain boundaries can lead to a spectrum that includes X-rays from more than one phase, resulting in poor mineral identifications. Arsenopyrite, the highest mean Z mineral of the major mineral phases, was consistently found to be lower by about 5% m/m when measured by EDS than when measured by XRD or WD-XRF (Figure 6) with moderately poor R² values of 0.69 and 0.41 for XRD and WD-XRF, respectively (Figure 7). The mismatch for arsenopyrite was much greater for EDS-XRF than for EDS-XRD, based on the slopes of 0.5 and 0.96 for WD-XRF and XRD, respectively in Figure 7. Additionally, arsenopyrite by EDS was moderately anti-correlated with the WD-XRF GOA. It is possible that the smaller interaction volume of the arsenopyrite contributed to a smaller area of the EDS analysis region being assigned to it as compared with lower Z materials. That is, a small amount of epoxy surrounding a low-Z mineral would be "counted" as that mineral; high-Z minerals would be surrounded by a narrower region than lower-Z minerals. Thus, the smaller interaction volume of arsenopyrite would lead to decreased arsenopyrite phase assignments via EDS compared with lower Z minerals.

Some materials are beam sensitive, and in the case of carbonates, they can physically degrade under higher current analytical conditions (Lane and Dalton 1994). Figure S2 shows the effect that the thermal decomposition of calcite under varying beam current (Figure S2A, B) and voltage settings (Figure S2C, D) has on X-ray signal counts. The deleterious interactions of the electron beam with the sample can be minimised by selecting different voltages, shorter dwell times, and/or lower currents for the electron beam. A lower beam voltage results in a smaller interaction volume, thus less sample degradation in the case of the carbonates. A FEG-EPMA has the advantage of generating stable electron beams at high currents, in our case ~280 nA, chosen to optimise the EDS detector dead time. To mitigate the beam damage, we used short dwell times over 500 frames to generate adequate counting statistics for phase identification, rather than one frame with a long pixel dwell time.

Degradation of the carbonates upon analysis by the electron beam is another likely contributing factor to the poor agreement and lack of a systematic linear relationship (R² = 0.1) for the carbonate mineral abundances determined by the three methods. The presence of carbon-rich epoxy did not confound carbonate identification, as it could typically be distinguished by the presence of a C I peak. However, the identification of carbonates was complicated by the carbon coating of the sample prior to EDS analysis. Difficulties in carbonate identification were compounded by the generally low amounts of carbonate minerals present in samples considered in this study.

High sodium materials, such as albite, are also beam sensitive (Nielsen and Sigurdsson 1981). Na is subject to diffusion in minerals and glasses when impinged by an electron beam. This is due to both thermal and space charge layer effects (Goodhew and Gulley 1974, Spray and Rae 1995). As the sample heats up due to the beam, the Na-O bonds break, and free Na⁺ ions move to the space charge layer resulting in lower Na X-ray counts. At 20 keV, and ~280 nA of beam current, it is almost certain...
### Table 3.
Relative per cent differences between EDS and XRD and WD-XRF, respectively, with major phase goodness of agreement (GOA) score

|                | AS 346 | AS 352 | GS 403 | GS 405 | GS 406 |
|----------------|--------|--------|--------|--------|--------|
|                | XRD    | XRF    | XRD    | XRF    | XRD    | XRF    | XRD    | XRF    | XRD    | XRF    |
| Quartz         | 46     | 58     | 306    | 356    | -34    | 18     | -33    | 3.1    | -45    | -1.1   |
| Albite         | 210    | *      | *      | *      | 117    | 62     | 51     | 11     | 44     | -0.7   |
| Feldspar (Ca-rich) | -     | -      | -      | -      | -147   | -      | -      | -      | -      | -      |
| K-feldspar     | 11     | -60    | -      | -      | -      | -      | -      | -      | -      | -      |
| Clays          | -      | -      | -      | -      | -      | -      | -      | -      | -      | -      |
| Chlorite       | *      | *      | 478    | *      | -87    | *      | 11     | *      | 55     | *      |
| Muscovite      | -      | -      | -      | -      | 66     | 65     | 25     | 42     | 106    | 86     |
| Talcite        | -      | -      | -      | -      | -      | -      | -      | -      | -      | -      |
| Apatite        | -      | -      | -      | -      | -54    | -12    | -      | -13    | *      | -46    |
| Svanbergite    | -      | -      | -      | -      | -      | -      | -      | -      | -      | -      |
| Gypsum         | -      | -      | -      | -      | -      | -      | -      | -      | -      | -      |
| Biotite        | -      | -      | -      | -      | -      | -      | -      | -      | -      | -      |
| Carbonates, other | 190  | 39     | 136    | 200    | 49     | 74     | -51    | -33    | 10     | 68     |
| Calcite        | -      | -      | -      | -      | -      | -      | -      | -      | -      | -      |
| Magnesite      | -      | -      | -      | -      | -      | -      | -      | -      | -      | -      |
| Rutile         | -      | -      | 828    | *      | *      | -26    | *      | 69     | -56    | -39    |
| Fe oxide       | -      | -      | -      | -      | -      | -      | -      | -      | -      | -      |
| Ilmenite       | -      | -      | -      | -      | -      | -      | -      | -      | -      | -      |
| Chrome         | -      | -      | -      | -      | -      | -      | -      | -      | -      | -      |
| Arsenopyrite   | -      | -      | -      | -      | -      | -      | -      | -      | -      | -      |
| Pyrite         | -10    | -35    | -14    | 68     | -33    | -23    | 0.6    | 16     | -8.0   | -44    |
| Molybdenite    | -72    | -86    | 1.4    | -60    | -      | -      | -      | -      | -      | -      |
| Chalcopyrite   | 6.9    | 20     | -5     | -16    | -      | -      | -      | -      | -      | -      |
| Sphalerite     | *      | 82     | *      | -23    | -      | -      | -      | -      | -      | -      |
| Covellite      | 40     | -      | -      | -      | -      | -      | -      | -      | -      | -      |
| Fluorite       | -      | -      | -      | -      | -      | -      | -      | -      | -      | -      |
| GOA Score      | 54     | 54     | 15     | 32     | 28     | 9      | 18     | 17     | 54     | 33     |

|                | PG 601 | PG 603 | PG 604 | PG 606 | PG 607 |
|----------------|--------|--------|--------|--------|--------|
|                | XRD    | XRF    | XRD    | XRF    | XRD    |
| Quartz         | -20    | -11    | -4.2   | 19     | 11     | 8.1    | 20     | 19     | -16    | 9.1    |
| Albite         | 145    | 73     | 52     | 98     | 7.6    | -0.08  | -6.1   | 29     | 79     | 140    |
| Feldspar (Ca-rich) | -     | -      | -      | -      | -      | -      | -      | -      | -      | -      |
| K-feldspar     | -48    | -86    | -      | -      | -      | -      | -      | -      | -      | -      |
| Clays          | -      | -      | -      | -      | -      | -      | -      | -      | -      | -      |
| Chlorite       | 47     | 194    | -1.1   | 4.6    | 102    | 134    | -42    | 60     | -12    | 42     |
| Muscovite      | 93     | 65     | 37     | 22     | -41    | 7.8    | -17    | -3.2   | 51     | 14     |
| Talcite        | -      | -      | -      | -      | -      | -      | -      | -      | -      | -      |
| Apatite        | -      | -      | 114    | *      | 492    | *      | 441    | *      | 26     | -      |
| Svanbergite    | -      | -      | -      | -      | -      | -      | -      | -      | -      | -      |
| Gypsum         | -      | -      | -      | -      | -      | -      | -      | -      | -      | -      |
| Biotite        | -      | -      | -      | -      | -      | -      | -      | -      | -      | -      |
| Carbonates, other | -82  | -100   | *      | 1003   | *      | 170    | -45    | 389    | -83    | -59    |
| Calcite        | -35    | 33     | -61    | -18    | 23     | -69    | -31    | 135    | 523    | -      |
| Magnesite      | *      | -58    | *      | -59    | *      | *      | -11    | *      | -54    | -      |
| Rutile         | -      | -      | -      | -      | -      | -      | -      | -      | -      | -      |
| Fe oxide       | -      | -      | -      | -      | -      | -      | -      | -      | -      | -      |
| Ilmenite       | -      | -      | -      | -      | -      | -      | -      | -      | -      | -      |
| Chrome         | -      | -      | -      | -      | -      | -      | -      | -      | -      | -      |
| Arsenopyrite   | 94     | -0.7   | -3.5   | -54    | 31     | -12    | 18     | -29    | 97     | 31     |
| Pyrite         | 184    | -24    | 67     | -26    | 15     | -55    | -33    | -70    | -53    | -77    |
| Molybdenite    | -      | -      | -      | -      | -      | -      | -      | -      | -      | -      |
| Chalcopyrite   | -      | -      | -      | -      | -      | -      | -      | -      | -      | -      |
| Sphalerite     | -      | -      | -      | -      | -      | -      | -      | -      | -      | -      |
| Covellite      | -      | -      | -      | -      | -      | -      | -      | -      | -      | -      |
| Fluorite       | -      | -      | -      | -      | -      | -      | -      | -      | -      | -      |
| GOA Score      | 54     | 54     | 15     | 32     | 28     | 9      | 18     | 17     | 54     | 33     |

Taking GS403 for an example, quartz measured by XRD was 26% m/m and by XRD was 17.2% m/m or 34% lower than the amount measured by EDS. Likewise, quartz abundance determined by WD-XRF data was 30.7% m/m or 18% higher than the quartz abundance measured by EDS. Minerals detected by only one method for all samples have been omitted for clarity, but are included in the Table S5.

Values in bold are major minerals used to calculate the GOA score.

- indicates mineral not detected.

* Indicates mineral was detected by EDS, but not by the comparison method.
| GS 407 | GS 409 | GS 410 | GS 411 | GS 412 | GS 413 |
|-------|-------|-------|-------|-------|-------|
| XRF   | XRF   | XRF   | XRF   | XRF   | XRF   |
| -40   | -3.5  | -30   | 10    | -41   | 0     |
| 93    | 13    | -27   | -46   | 51    | 13    |
| -1.9  | 27    | -2.7  | 1.9   | -27   | 116   |
| 3.9   | -1.0  | -20   | -29   | 19    | -1.9  |
| -84   | 31    | -62   | 84    | 44    | 199   |
| -1.4  | -29   | 124   | 157   | -81   | 42    |
| -38   | 197   | -3.5  | -3.3  | -3.5  | -3.3  |
| 52    | -14   | -57   | -8    | -18   | *     |
| *     | 66    | -1.4  | -3.3  | -3.3  |
| *     | -56   | -54   |
| 12    | *     | *     |
| -83   | -40   | -91   |
| *     | -3.3  |
| -27   | -21   | -4.4  |
| 6.6   | -1.17 |
| -35   | -5    |
| -13   | -16   |
| -12   | -18   |

| PG 608 | PG 609 | PG 610 | PG 612 | PG 621 | PG 622 |
|--------|--------|--------|--------|--------|--------|
| XRF    | XRF    | XRF    | XRF    | XRF    | XRF    |
| 11     | -4     | 4.4    | -7.2   |
| 95     | 140    | 15     |
| -86    | -83    | -68    |
| -29    | 146    | -61    |
| 24     | 31     | 42     |
| 6.9    | 38     | -66    |
| *      | 1.38   | *      |
| *      | 1381   |
| -64    | -2.4   |
| -3.5   | -100   |
| 77     | 219    |
| -12    | -47    |
| *      | *      |
| -1.4   |
| 17     | 15     |
| -51    |
| -68    |
| -1.4   |
| 35     | -13    |
| 48     |
| 52     |

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that the Na X-ray counts were depressed from the true values leading to an under-assignment of albite for the EDS phase assignment. Additionally, Na X-rays are absorbed heavily by the sample, leading to poor Na peak counting statistics. Both of these effects could have led to albite being systematically assigned to another phase, most likely another feldspar. This would be consistent with the higher amounts of albite determined by XRD (1.5% m/m) and WD-XRF (2.9% m/m) as well as the calculated moderate correlation of Na2O with the XRD GOA for the PG.

Figure 6. Comparison of mineralogical abundances of major phases from EDS phase mapping, XRD and WD-XRF. Major phases present at greater than five per cent weight abundance are plotted. EDS results are the mean of three analysis areas per sample. Abbreviations as Table S1. The Carb category is the sum of ankerite and dolomite.
Figure 7. EDS mineral phase abundance vs. XRD and WD-XRF mineral phase abundance regressions. Shading represents the 95% confidence intervals. Regressions for chalcopyrite were of limited utility consisting of only two and three data points for XRD and WD-XRF, respectively, and hence have been omitted for clarity.
subsample. The GS subsample consistently had more albite, which likely minimised this effect.

In the case of albite, a higher beam voltage shifts the space charge layer deeper and is shielded from the Na+ ions resulting in minimised Na migration (Nielsen and Sigurdsson 1981), despite the very high current density (Morgan and London 2005). Because we were interested in exciting the transitions metals, we opted for a 20 kV beam. In retrospect, arguments for both lower and higher beam voltages could be made. A lower beam voltage might have been a better choice given the large amount of lower-Z minerals present in most of our samples. A higher beam voltage might have been a better choice to mitigate sodium migration as well as exciting higher energy X-rays for improved phase identification.

**Solid solution minerals, XRD fitting, and WD-XRF calculations**

Solid solution minerals have fixed end-member compositions, but also may have compositions that vary continuously between end-members. These solid solution mineral series, such as chlorite, biotite and the feldspars complicate calculation of mineral abundances because it is difficult to know what the precise mineral composition is in a given sample. While for the most part we were able to confidently assign these phases via EDS into mineral type, the solid solution problem presents some challenges when attempting to validate the EDS results with XRD and WD-XRF. K-feldspar, handled as the pure KAlSi3O8 end-member seems to be the most successful mineral phase with excellent agreement, while albite, muscovite and chlorite have poorer agreements for at least one technique comparison parameter (R², slope, intercept; Figure 7). Solid solution minerals also complicate the selection of the best reference SRD pattern and the correct composition assignment for WD-XRF mineral calculations. These factors, in conjunction with the low abundance of chlorite, contributes to very poor regression relationships between EDS and the other two methods for this solid solution mineral series.

The coefficients of determination for the regression comparing EDS with XRD and WD-XRF for chlorite and muscovite were less than 0.32, with slopes of < 0.6 for both XRD and WD-XRF. Chlorite is typically a minor phase in these samples, further complicating its identification and quantification by XRD. The diagnostic XRD peaks for chlorite and muscovite are at low 2theta. Small adjustments in background fitting can affect the ‘best’ fitting diffractogram that most closely represents the solid solution present as well as the calculated abundance of the mineral. Additionally, the phyllosilicates are subject to strong preferred orientation effects which are a major driver in their uncertainty by XRD (da Silva et al. 2011). These effects combine to make it challenging to model with only one to two diagnostic low angle peaks and the other peaks obscured by overlap with major phases at higher angles. A poor pattern match would lead to poor Rietveld fit. Furthering the challenge of background fitting, iron-rich samples will fluoresce when analysed with a Cu XRD radiation source, and this leads to higher background intensities (Coetsee et al. 2011). Many of our samples are iron rich, and this made the background fitting more challenging, further affecting chlorite and muscovite quantification.

Quartz and the carbonate minerals are dominated by single diagnostic peaks in XRD. Quartz as measured by XRD is consistently about 3.7% m/m lower than EDS. It is very difficult to fully match the shape of the main quartz diffraction peak. Rietveld refinement minimises the residual of the entire pattern, and this can appear to lead to consistent under-abundance of quartz by XRD compared with the other methods. Additionally, the presence of amorphous SiO2 may contribute to higher quartz abundances measured by EDS. In the case of the carbonates, the single diagnostic peaks can be difficult to fit with confidence when present at low concentrations in complicated samples.

The EDS data demonstrated that the chlorite was Fe-rich. This was consistent with the XRD data that showed unit cell parameters and relative peak heights consistent with the presence of an Fe-rich chlorite. Iron is problematical in these samples for WD-XRF mineral recalculations as it is present as FeS2 in pyrite, an Fe oxide, and potentially as Fe3+ and Fe2+ in the iron-rich chlorite. Dividing up iron among these phases requires high accuracy in all of the elements. Our calculations do not result in unique solutions of mineral abundances, and we informed how much of an element we assigned to a given mineral phase with insight from the EDS and XRD results. A further challenge is that arsenopyrite is not stoichiometric, and the true concentration of As in its formula of FeAs(1+/−x) S(1−+/−x) is an unknown. This could contribute to the disagreement between the mass fraction values for arsenopyrite calculated from WD-XRF (calculated for FeAsS) and EDS data. The EDS data indicate and the XRD data confirm the presence of muscovite (K:Al molar = 1:3), albite, and K-feldspar (K:Al molar = 1:1), with small amounts of other Al-bearing minerals. If all three phases are modelled as pure (no solid solution), then all Na is assigned to albite and the remaining K and Al are combined in such a way that all of both elements are used up. This procedure is sensitive to the uncertainties in all three elements and could explain the poor regression of EDS muscovite vs. WD-XRF
muscovite, and the systematic K-feldspar is lower by WD-XRF compared with EDS. The remaining SiO$_2$ is assigned to quartz, which will be affected by any errors in the previous step. This could be a cause of the increase in quartz by WD-XRF over that found by EDS. This approach does not take into account the substitution of trace elements into a given mineral (e.g., Ti in quartz), although the effects of trace element substitutions will be minor except (possibly) in the case of very high abundance minerals.

**Sample size particle statistics**

A most significant outcome of the bivariate correlations between the GOAs and the N (number of particles) was the strong correlation between the XRD GOA and N for the PG subset (Table S7). As N increases, the XRD GOA increases, indicating worse agreement between the techniques. No correlation or anti-correlation of any strength exists for the WD-XRF GOA (Table S8). These samples, as mill products, were of various degrees of fineness, having already been ground as part of the extraction process. This cannot be attributed to particle size effects from the electron beam, as the correlation is only present for the XRD GOA (Gattlieb et al. 2000). We believe this effect is from the samples being over ground by the combination of mill processing and micronising, leading to a loss in peak intensity and poorer XRD GOA (O’Connor and Chang 1986). This is consistent with the moderate anti-correlation of the mean of the log-transformed particle size distribution and the XRD GOA.

Parameters describing the population statistics of the distribution of the log-transformed particle sizes greater than 1.5 µm revealed correlations with the XRD GOAs. Samples that had larger particle sizes to begin with, with the distribution pushed to larger particle sizes, given by the shifted median, yielded a better XRD GOA. This indicates that the PG subset was more finely ground to start with compared with the GS samples. Given that not all minerals have the same grindability, this effect is likely exacerbated between soft, tiny, minerals (e.g., the phyllosilicates) and bigger, harder, minerals. It is also further exacerbated by 2D image analysis overestimating the volume of smaller particles compared with the true size of the 3D particles (Jones 1987, Califice et al. 2013).

**Trace mineral identification**

One distinct advantage of the EDS technique is its capability to identify trace phases. Unique mineral phases present in particles less than the minimum size threshold are not assigned a phase during the Xphase extraction. If the unassigned grains stand out visually, they can be identified offline using the spot analysis tool on the EDS data cube. For example, we were visually able to identify fine-grained high mean $Z$ minerals, as these minerals show up as saturated pixels in the BSE images. In nearly every analysis region we were able to identify barite, even when not identified by the EDS software. Additionally, the EDS was able to detect low abundance phases such as ilmenite, biotite, maghemitite, feldspar, tetrahedrite, titanite, svarnerbite, chlorapatite, and a Cr-rich phase. These minerals were too low in abundance to be detected by XRD, and intractable to calculate from the WD-XRF data without complementary knowledge of the phases present.

By doing the EDS analysis in conjunction with the XRD and WD-XRF phase analysis, each approach improves the results of the other. Knowing what the suite of minerals in a sample are present from XRD analysis was useful in identifying minerals in the subsequent EDS data. We were able to take the minor mineral phases found by EDS, and add those minor mineral phases into the Rietveld refinement. This improved the fit of the Rietveld refinement, although minor mineral phases with few characteristic XRD peaks such as barite and calcite were not able to fitted even when identified with EDS. The small number of small peaks associated with barite and calcite were indiscernible due to peak overlaps of the major minerals in the diffractogram.

In many ways WD-XRF is ‘too’ sensitive an instrument: elements present at $\mu$g g$^{-1}$ levels may be present in the bulk as trace concentrations in a major or minor mineral phase or as low abundance element-rich minerals. These low abundance minerals cannot be detected as separate minerals by XRD and are unlikely (given counting statistics) to be found by the EDS phase mapping. For example, Mo was identified with mass fractions of about 30 $\mu$g g$^{-1}$ in several samples. Most likely this is present as the mineral molybdenite (MoS$_2$), the most common Mo-bearing mineral, but at mass fractions too low to be identified by the other methods. Molybdenum could also be present at trace levels in the more common mineral phase pyrite, but Mo also would not be detected by either the XRD or EDS phase mapping. Similarly, the WD-XRF also detected Pb and As in low mass fractions in some samples; again, these elements could be present at trace levels in another more abundant sulfide phase, but they are most likely present as galena (PbS) and arsenopyrite (FeAsS), respectively, but at abundance levels below detection by the other methods.

**Is EDS phase mapping representative?**

An additional challenge for using EDS for bulk mineralogy is discerning how representative a single field of view
is relative to the entire billet or bulk sample. A given billet of these samples was likely to have an analytical area of \( \sim 5 \text{ cm}^2 \). A given phase map typically measured between 0.17 and 1.1 mm\(^2\) (depending on the magnification) is equivalent to between \( \sim 0.034\% \) and 0.22\%, respectively, of the analytical area. The presence of an atypical distribution of grains is likely to skew the mineralogical abundance data. Given the broad agreement between the EDS approach, and results from XRF and XRD (Figure 6 and Table 3), as well as the generally strong linear correlations (\( R^2 \)), minimal offset (y-intercept), and good agreement (slope) shown in Figure 7 for most major minerals, EDS phase mapping appears to be representative for determining major phases in the absence of very large nugget grains of minor phases for fine-grained samples. The effect of nuggets could be mitigated by grinding or sieving samples.

**Considerations for using EDS phase mapping**

The ideal sample for EDS phase mapping would have: (1) mineral grains that are larger than the beam interaction volume, but still small and with a small range of grain sizes to yield a large number of observations; (2) no large nuggets of low abundance minerals; (3) minimal beam sensitive minerals, such as the carbonates and Na-rich minerals like albite. Minerals with a lower \( Z \) will be overestimated compared with higher \( Z \) minerals. If grains in the sample are not well sorted, the minerals that are present primarily as smaller particles will be overestimated compared to minerals present predominantly as larger particles. Caution or complementary analyses are warranted when sample characteristics deviate from these ideal characteristics. Despite these challenges, the EDS typically agreed with other techniques within 10% for major minerals.

**Conclusions**

Using EDS phase mapping on three fields of view is sufficient to obtain an estimate of bulk mineralogy of a sample. The results for minerals present at greater than 5% m/m are broadly similar to those obtained by XRD or mineral recalculation WD-XRF. Additionally, EDS phase mapping has the advantage of being able to identify, but not quantify, minor and trace phase. EDS phase mapping is not subject to user error in discerning the initial phases based on X-ray peak identification and requires no a priori knowledge of the sample. However, the user’s mineralogical knowledge will be needed to make the final mineral phase identification. It does rely on the user to make appropriate judgements and use EDS best practises once the phases are produced to identify the minerals correctly. EDS phase mapping could be further validated by analysing mixtures of minerals with known abundances, as well as comparing with electron back scatter diffraction (EBSD) results.

Care should be taken in interpreting results for samples with particles smaller than the interaction volume of the electron beam, samples that have beam sensitive minerals for a given beam voltage, and samples with the presence of large mineral grains of minor phases. While EDS phase mapping is computationally intensive, there are time savings if samples have already been prepared as polished thin sections, with analysis taking less time than preparing and analysing a separate subsample for XRD and/or WD-XRF analysis.

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**Data availability statement**

Data are available from the corresponding author with permission of Barrick Gold, ASARCO, and Northern Star Resources. Python code for sorting ImageJ output is available at https://github.com/jspaleta/python-rock-grain-graphing.

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Supporting information

The following supporting information may be found in the online version of this article:

Figure S1. Log transformed particle size distributions.

Figure S2. Effect of varying beam conditions on calcite.
Table S1. Mineral names and chemical formulae discussed in text.

Table S2. Weight per cent mineralogical abundance from XRD data.

Table S3. XRF oxide and element mass fractions.

Table S4. Weight per cent mineralogical abundance calculated from WD-XRF Omnan data and normalised to 100%.

Table S5. Relative per cent differences between EDS and XRD and WD-XRF, respectively, with all minerals detected and with major phase Goodness of Agreement (GOA) score.

Table S6. Particle size distribution statistics of the log transformed distribution of sample particle areas.

Table S7. Correlation of XRD GOA scores with EDS particle size statistics, EDS mineral abundance, major element mass fractions from WD-XRF, and minerals from XRD.

Table S8. Correlation of WD-XRF GOA scores with EDS particle size statistics, EDS mineral abundance, and major element mass fractions from WD-XRF.

Appendix S1. Calculation of the Goodness of Agreement (GOA) metric.

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