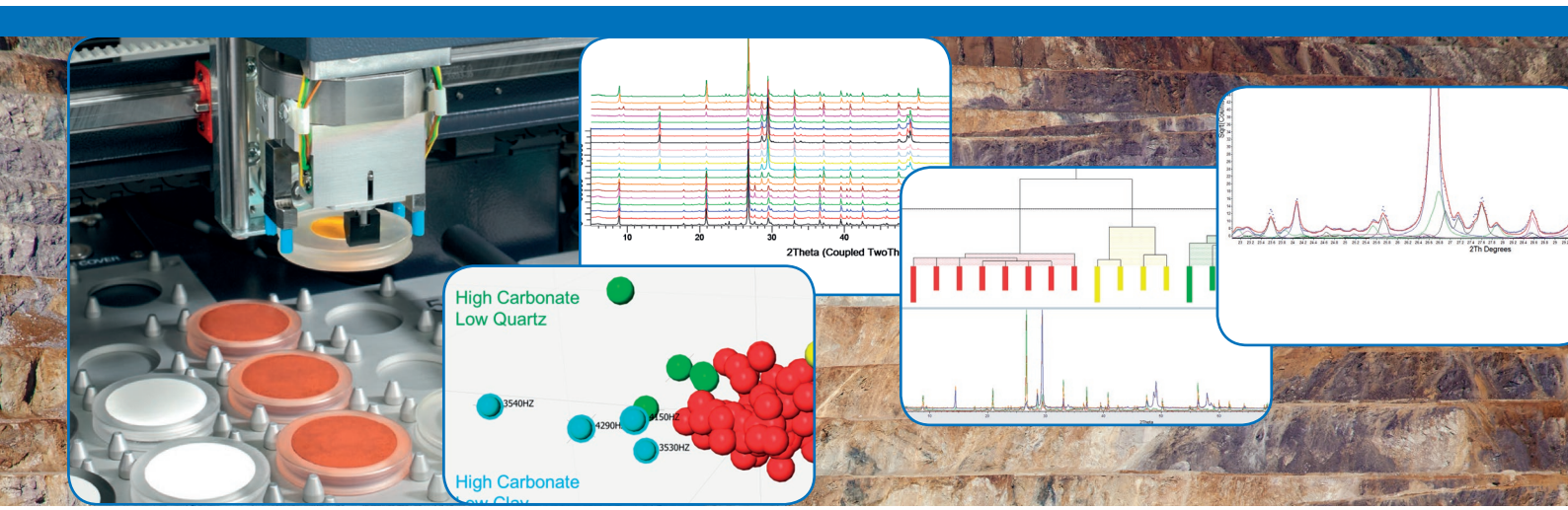


Lab Report XRD 86

# XRD in Mining:
# Standardless Processing of Large Datasets with Rietveld Refinement and Cluster Analysis


## Abstract

X-ray diffraction (XRD) provides a wealth of structural information, particularly in naturally occurring geological formations where multiple phases may be present in the same sample. Mining and drilling operations with high sample throughput can benefit from standardless analysis tools, particularly in cases where the majority of samples possess similar compositions. These tools include batch processing of quantitative mineralogy (DIFFRAC.TOPAS) and clustering of diffractograms (DIFFRAC.EVA).


## Introduction

XRD is a powerful technique for structural analysis of mineralogical species. In addition to providing for the identification of distinct crystalline phases and polymorphs, analysis by XRD also enables quantification of complex mixtures and the detection of structural changes, such as lattice expansion in swelling clays and cationic substitution in carbonates. For complete unknowns, data analysis is typically approached in two-steps: (1) phase identification by matching observed reflections to a database of known patterns and (2) quantification of selected phases, frequently with Rietveld refinement, using structural information for each identified phase.


Figure 1. D8 ENDEAVOR process diffractometer.

Exhaustive processing of individual diffractograms, however, is beyond the scope of many mining operations, particularly in automation environments and at sites that generate a large volume of data. Here, the primary goal might be routine analysis for quality control or the identification of statistical outliers.

In this report, we describe the analysis of two distinct sets of mineral samples – shale rock formations and copper ore bodies. In the former, varying clay and carbonate concentrations might lead to specific steering decisions or well treatments. In the latter, diffraction studies might be applied to identify higher concentration regions of desirable ore minerals.

A separate refinement model was developed for each sample set and then applied to each diffractogram via batch processing with DIFFRAC.TOPAS. Quantitative Rietveld methodologies are exceptionally powerful and can account for a large number of variables, including preferred orientation effects, contrasts in absorption, and peak broadening associated with disorder or crystallite size reduction. Crystallographic information can be imported from literature references or structural databases, making it possible to quantify mineral mixtures even in the absence of physical standards. Well-defined models are extremely robust and can quickly process large numbers of scans.

Both datasets were also processed using the clustering algorithms in DIFFRAC.EVA. In a sense, this can be considered a "standardless" approach, where no information is known or applied with regards to specific crystalline phases. Rather, in this situation, scans are assigned to groups based on similarity, making it possible to quickly and easily identify samples of interest. For example, outliers might be flagged in a quality control setting for having significant variation in peak location or aberrant peak intensities. DIFFRAC.EVA allows prescreening of > 10,000 scans and single dataset clustering of up to 2,000 patterns, making this a useful tool for high-throughput analysis and rapid identification of patterns that merit more detailed evaluation.

## Experimental

Samples were prepared by wet-milling in ethanol with a McCrone micronizing mill and agate media. Diffraction specimens were prepared from the fine powders using back-loading sample holders to minimize the effects of preferred orientation.

Data were collected using the D8 ENDEAVOR (Figure 1) process diffractometer equipped with a motorized anti-scatter screen and robotic sample handling. The D8 ENDEAVOR is a floor-standing instrument that excels in a dedicated laboratory environment and is capable of handling up to seventy-two (72) samples per load. The diffractometer was equipped

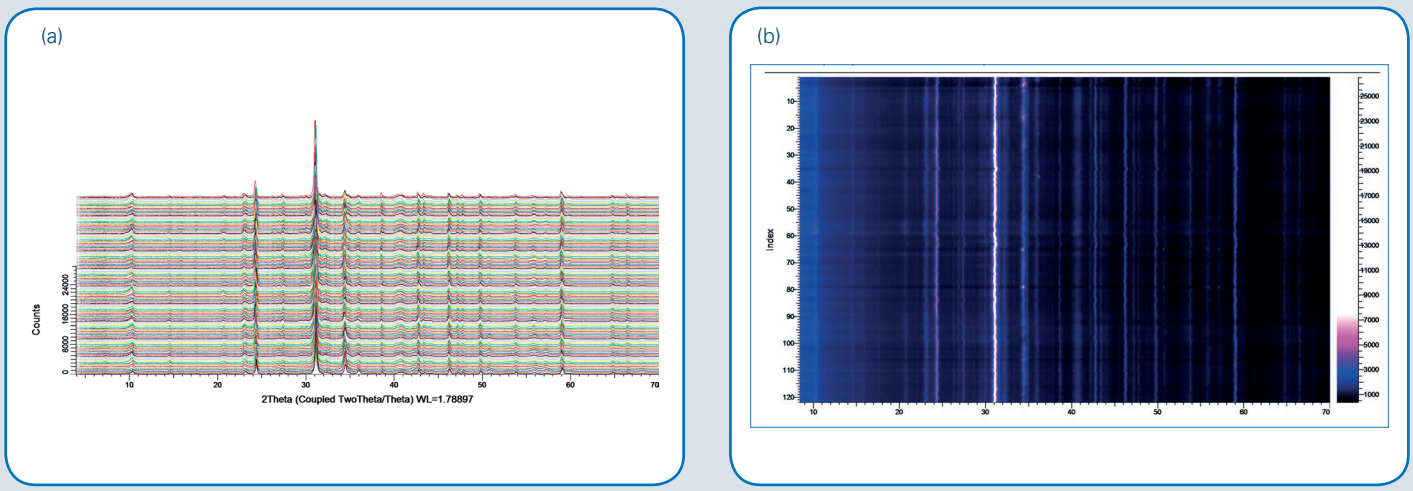


Figure 2: (a) Waterfall plot and (b) 2D intensity map of data collected from shale rock cuttings. Diffractograms demonstrate similarity in both observed peak locations and intensities, indicating similar mineralogical compositions.

with a LYNXEYE XE silicon strip detector, which enables rapid data collection and suppression of sample fluorescence. Scans were collected in coupled Theta/Theta mode, allowing the samples to stay horizontal during data collection and minimizing sample spillage and cross-contamination.

## Analysis

Phase identification was performed using DIFFRAC.EVA in conjunction with the ICDD PDF-4+ database. Data visualization was handled using the graphical functionalities and cluster analysis tools in DIFFRAC.EVA. Identified crystalline phases were quantified using Rietveld analysis with DIFFRAC.TOPAS.

### Case Study: Shale Rock Analysis

This work expands on a previous study of shale rock in the Duvernay formation. Initial studies focused on the development and testing of quantification models with a limited number of samples. Data presented here represents drill cuttings taken in 10 m intervals over 1200+ m in a horizontal well.

Collected data are shown in Figure 2. Viewing as a waterfall plot highlights the similarities in observed diffraction events, indicating concomitant similarities in mineralogical composition. Differences in peak intensities can be observed in the 2D intensity map, with several noticeable bright spots associated with the most intense calcite reflection (1 0 4).

Several sets of outliers are identified when processing through the clustering algorithms, as shown in the metric multidimensional scaling (MMDS) view shown in Figure 3. The majority of samples are clustered into the red group, indicating a high degree of data similarity. Several outliers are assigned to separate clusters: unsurprisingly, many of these are samples with more intense diffraction from calcite. This demonstrates the ease with which clustering approaches can quickly identify statistically different specimens, even in the absence – or prior to – detailed crystallographic analysis.

The refinement model developed in the previous study was applied via batch processing with DIFFRAC.TOPAS. Results for phase quantification are output in tabular format and can be easily converted to mineralogy tracks (Figure 4) using third-party software. A detailed investigation of the blue and green clusters reveals calcite concentrations ranging from 17-38 wt% in contrast to the average calcite value for all samples (10 wt%).

### Case Study: Copper Ore

In this case study, twenty samples of copper ore were taken from various mine site locations and analyzed for compositional variance. As these samples did not have a prior quantification model, crystalline phases were first identified with DIFFRAC.EVA and then added to a fresh refinement model in DIFFRAC.TOPAS. Diffractograms were handled in similar fashion to the shale rock samples (i.e., clustering by similarity and batch quantification using a single model).

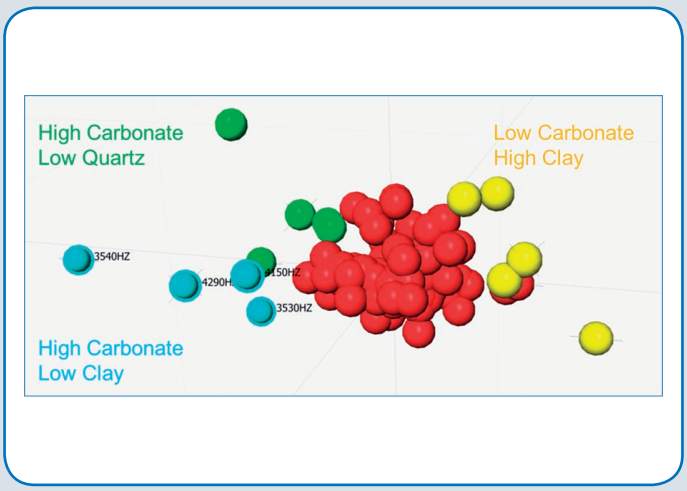


Figure 3: 3D MMDS plot for cluster analysis and data similarity. The majority of samples are assigned to the central (red) group, indicating strong correlation. Groups assigned to blue and green are identified at statistical outliers, which correspond to higher calcite concentrations relative to the average.

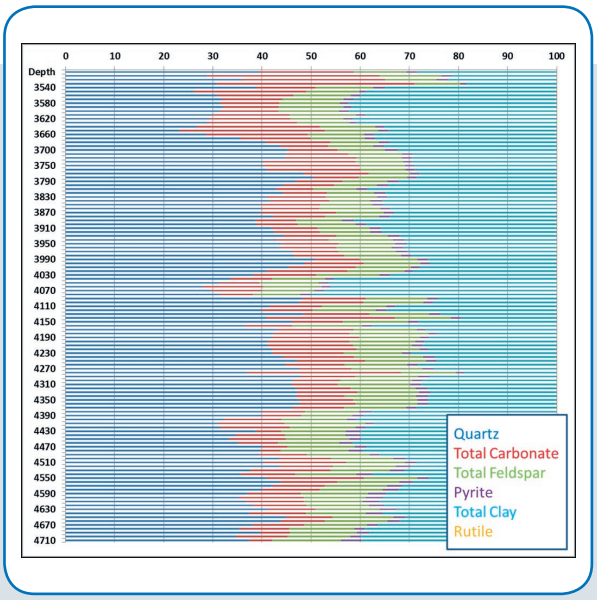


Figure 4: Mineralogy track for all shale samples generated by batch processing with Rietveld refinement. Phase quantification is plotted along the x-axis, and measured depth is plotted along the y-axis.

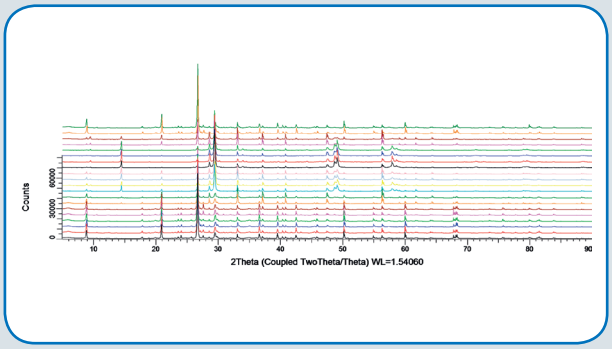


Figure 5: Waterfall plot for data collected from copper ore samples. Stark differences in relative peak intensities indicate large compositional variances.

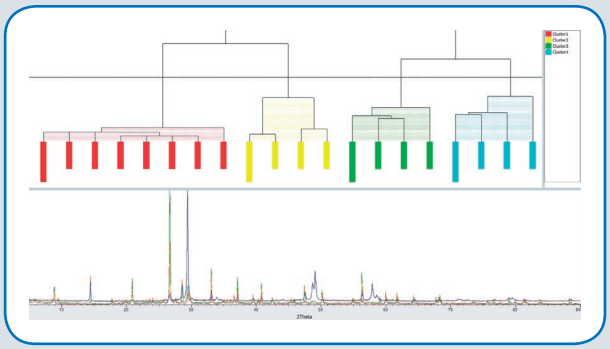

Figure 6: . Dendrogram plot for cluster analysis of copper ore samples, indicating four distinct groups. Selected diffractograms are shown below the dendrogram for reference, highlighting the differences in diffraction data between groups.

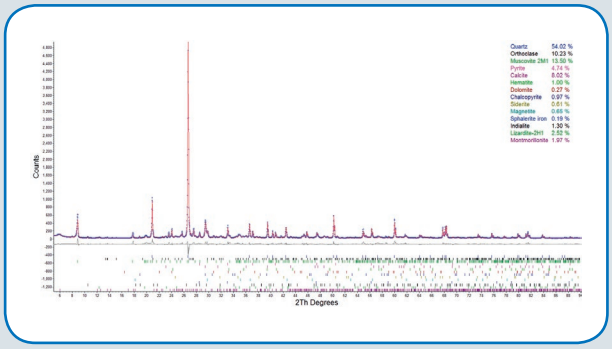


Figure 7: Quantitative Rietveld refinement with DIFFRAC.TOPAS for a single copper ore sample. The contribution of each mineralogical phase to the total diffraction pattern is indicated in the colored traces below the diffractogram.

| | Total Average | Red Average | Yellow Average | Green Average | Blue Average |
|---|---|---|---|---|---|
| Quartz | 31,4 | **49,9** | 33,5 | 19,7 | 3,9 |
| Pyrite | 12,1 | 4,7 | **23,7** | 17,3 | 10,3 |
| Chalcopyrite | 18,6 | 2,3 | 7,1 | **28,9** | 52,3 |

Table 1: Quantification for selected minerals with calculated averages for each identified cluster.

All collected diffractograms are shown in a waterfall plot in Figure 5: unlike the previously discussed shale cuttings, there are quite obvious differences in diffraction data. Clustering assigns the data into four distinct groups, as shown in the dendrogram plot in Figure 6. A representative diffractogram for each cluster is shown below the dendrogram, highlighting the significant differences in peak intensities for a number of reflections, which in turn indicate considerable variance in composition.

Quantitative Rietveld refinement of a single sample is shown in Figure 7. Identified phases include common minerals, such as quartz and calcite, as well as ore minerals, such as chalcopyrite. A single refinement model was applied to each diffractogram and weight percentages exported in tabular format.

In-depth Rietveld analysis reveals strong correlations between composition and clustering. Selected phases and weight percentages are shown in Table 1. The yellow cluster, for example, has an average pyrite content of 23.7 wt%, which is more than double the average concentration for all samples (12.1 wt%). Chalcopyrite is an even more dramatic example of clustering effectiveness: green and blue groups both have a considerable amount of this mineral (28.9 and 52.3 wt%, respectively). Red and yellow groups are both well under 10 wt%. This initial study establishes a firm basis for future analysis within this specific mining locale, as an expanded sample set can be easily sorted based on similarity to existing clusters. This can be done fully automatically and an expert knowledges is not required.

## Conclusions

Characterization of high sample volumes presents a number of unique challenges and can benefit from software tools designed to handle large datasets. By combining clustering approaches and batch processing of refinement models, it is possible to quickly handle a large number of diffractograms, identify outliers or samples of interest, quantify mineral content, and draw correlations between sample groups.

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