*Paper 86*

# Modern X-ray Diffraction Techniques for Exploration and Analysis of Ore Bodies

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## ABSTRACT

*X-ray diffraction (XRD) can provide useful information about the composition of an ore sample in terms of quantification of crystalline phases and also amorphous content. XRD is also a powerful technique for studying substitutional solid solutions that can affect mining productivity, such as determining lattice bound aluminum in Goethite. Knowledge of the phases present can predict processing required to beneficiate the ore (flotation, magnetic separation, etc), or further upstream can dictate the best ore bodies to mine. In the analysis of iron ore, XRD can identify the phases containing iron, such as Hematite Fe2O3, Magnetite Fe3O4, and Goethite FeO(OH), and any other mineral phases present, especially silicas. Quantitative analysis is possible by various classical methods such as straight line or polynomial calibration with standards, but modern quantification analysis techniques such as Rietveld analysis or full pattern autoscale analysis are attractive alternatives, as they do not require any standards. These methods offer impressive accuracy and speed of analysis. The Rietveld method compares calculated vs. experimentally derived X-ray powder diffraction patterns for a phase, adjusting a wide-variety of crystallographic-, chemical- and modal-abundance parameters until the two are in agreement. Another analysis technique offering great benefit to ore exploration is cluster analysis. This technique greatly simplifies the analysis of a large amount of data from e.g. drill core samplings, and automatically sorts closely related scans of an experiment into separate clusters and marks the most representative scan of each cluster as well as outlying patterns. This can facilitate multi-dimensional compositional mapping of ore deposits, identifying regions of favorable mineral composition. A case study of the XRD analysis of hexagonal and monoclinic pyrrhotite phases, which are often associated with base and precious metal ore bodies, will be presented, with comparisons to other analytical techniques. Understanding the ratios of these phases is an important component of any study relating the genesis, mineral distribution and subsequent beneficiation of magmatic ores. Details of the techniques used, sample optimization methodologies, results, data precision and limitations will be discussed. The approaches have enormous potential as an inexpensive, reliable tool, useful in the characterization of ore materials from any geological environment.*

## X-RAY DIFFRACTION

X- ray powder diffraction (XRD) is a versatile, non- destructive analytical method for identification and quantitative determination of crystalline phases present in powder and solid samples. Identification of phases is achieved by comparing measured data to a reference database, the most comprehensive of which is maintained by the International Centre for Diffraction Data (ICDD). This decades old technique has been a standard technique for qualitative analysis of mineralogical phases, but quantitative methods were often difficult when the technique called for pure phase standards. The reference intensity ratio (RIR) method is a quantification method that can give a quick analysis, but is subject to inaccuracy due to preferred orientation of crystals in the sample.

Modern quantification analysis techniques such as Rietveld analysis or full pattern autoscale analysis are attractive alternatives, as they do not require any standards. These methods offer impressive accuracy and speed of analysis. Modern XRD equipment is also capable of producing data of sufficient quality for Rietveld analysis in just minutes, instead of an hour or more with traditional detectors; making it more amenable to process control.

## Rietveld Analysis

The Rietveld method compares calculated vs. experimentally derived X-ray powder diffraction patterns for a phase, adjusting a wide-variety of crystallographic-, chemical- and modal-abundance parameters until the two are in agreement. The Rietveld method is a full-profile (rather than single peak), diffractogram-fitting technique that generates calculated diffractograms and attempts to match these to experimentally derived ones. It operates by calculating a theoretical

diffractogram for a given phase, then proceeds through a series of least-squares iterations wherein a variety of experimental (e.g. background, two-theta displacement) and physical (e.g. unit-cell parameters, site-occupancy factors) parameters are varied until a defined convergence value (goodness of fit; GoF) is obtained.



**Figure 1:** Modern XRD equipment such as this from PANalytical incorporate computer controlled slit optics, a variable speed spinner stage, and a solid state X'Celerator detector to produce high resolution data in a fraction of the time traditionally required – up to 100 times faster.

The intensity of the $k^{th}$ Bragg reflection, $I_k$, is given by the expression:

$$I_k = S \ M_k \ L_k \ [F_k]^2 \qquad (1)$$

Where S is the scale factor, $M_k$ is the reflection multiplicity, $L_k$ is the Lorentz-Polarization factor, and $F_k$ is the structure factor:

$$F_k = \sum_{j=1}^{n} f_j \ exp \ (2 \ \pi \ I \ h_k^t r_j - h_k^t B_j \ h_k) \qquad (2)$$

Where $f_j$ is the scattering factor atom j, $h_k$ is a matrix representing the Miller indices, $r_j$ is a matrix representing the atomic coordinates, $B_j$ is a matrix representing the anisotropic displacement parameters, and t represents the transpose of the matrix.

The result is a calculated X-ray diffraction profile that best fits an experimental one, both in terms of intensity, peak position and peak shape. For samples with amorphous content, a known quantity of an internal standard may be incorporated in the sample to calculate a weight fraction of amorphous content in addition to quantifying the crystalline phases.

The strengths of the Rietveld method are:
1. Suitable for homogeneous or heterogeneous samples;
2. Works with powdered materials;
3. Relatively fast;
4. Cost-effective;
5. Effective at distinguishing between phases that may only differ subtly from one another;
6. Capable of producing quantitative modal abundances for the phases being analyzed (down to < 1 %).

Some limitations of the Rietveld method include:

1. requires atomic structure of phase to be known;
2. If phases are missing, the results are relative weight percentages, not absolute weight percentages;
3. Sometimes difficult to extract modal data for samples containing two or more minerals of the same family (*e.g.* amphiboles);
4. Best results are obtained when one has an understanding of mineralogy, crystallography and both the overall philosophy and approach to a successful Rietveld analysis.

## Case Study 1: Iron Ore Analysis

XRD is a powerful technique for the analysis of iron ore because it can tell you what phases contain Fe, e.g. Hematite $Fe_2O_3$, Magnetite $Fe_3O_4$, or Goethite FeO(OH); it can identify other mineral phases present, especially silicas, and can provide quantitative analysis of all phases. Also, knowledge of the phases present can predict processing required to beneficiate the ore (flotation, magnetic separation, etc).

As a demonstration of the accuracy of the Rietveld standard less analysis technique, a sample of NIST SRM693 Iron ore from Labrador was measured in less than 5 minutes on a PANalytical X'Pert PRO MPD diffractometer and analyzed by Rietveld. The results compared very closely for total iron content to the certificate of analysis provided by NIST.

**Table 1: Calculated iron content and certified iron content.**

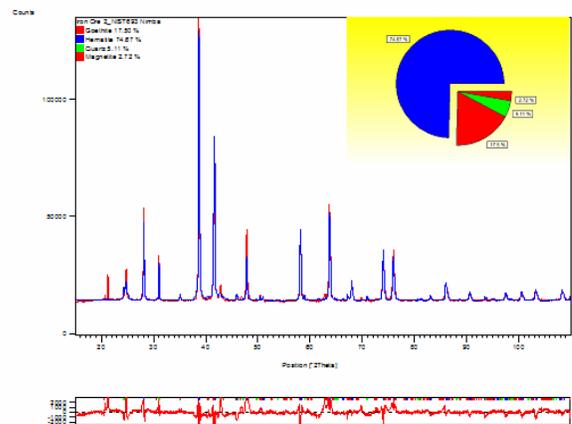| Phase | % by Rietveld | Fe% in phase | Total Iron |
|---|---|---|---|
| Hematite | 74.57 | 70% | 52.27 |
| Magnetite | 2.72 | 72.4% | 1.97 |
| Goethite | 17.5 | 62% | 10.85 |
| Total Fe in ore | | | 65.09% |
| Total Fe by NIST Certificate of Analysis | | | 65.11% |



**Figure 2:** Rietveld analysis of NIST SRM 693 iron ore from Labrador.

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An iron ore sample supplied to a steel production plant was analyzed by Rietveld analysis for composition, and these values were also compared to those generated by the RIR method. The data was collected on a PANalytical X'Pert PRO  MPD system using Cobalt radiation.  This type of radiation is especially suited to iron bearing materials, as it produces high resolution data unhampered by the sample fluorescence which is an issue for Copper radiation.  The measurement took eight minutes. Four phases were identified: cohenite, iron, wuestite, and magnetite.  The enlarged region of the diffraction pattern in Figure 3 shows how well the Rietveld calculated pattern explains all of the intensity seen in the measured pattern. The RIR values are fairly close to the Rietveld calculated weight fractions, but do not take into account any preferred orientation.
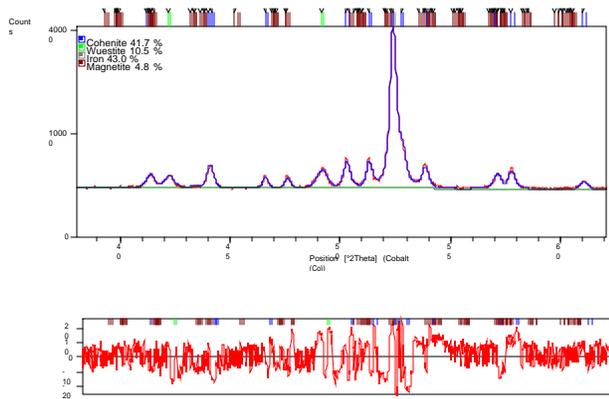


**Figure 3:** A portion of the Rietveld simulation overlaid with the measured data.

**Table 2: Comparison of Rietveld and RIR quantification.**

| No. | Phase | Rietveld % | RIR % |
|-----|-------|-----------|-------|
| 1 | Cohenite | 41.7 | 42 |
| 2 | Wuestite | 10.5 | 6 |
| 3 | Iron | 43.0 | 45 |
| 4 | Magnetite | 4.8 | 7 |

### Case Study 2: Cluster analysis of bauxite

Modern X-ray diffraction equipment like X'Pert PRO systems with a n X'Celerator detector allow the rapid collection of hundreds of scans in very short time. This can be useful in an application area such as drill core analysis. Cluster analysis is a method that uses statistical methods to greatly simplify the analysis of large amounts of data by:

1. Automatically sorting all scans of one or more experiments into classes of closely related scans.
2. Identifying the most representative scan of each class.
3. Identifying the two most different scans of each class.

4. Identifying outliers not fitting into any class.
5. Allowing visual inspection of the clustering by plotting the principle components analysis (PCA) score

A set of 17 bauxite samples was analyzed by X-ray diffraction and subsequently processed via cluster analysis. The results showed all patterns fell into three distinct clusters – one high in gibbsite, one high in quartz, and one high in kaolinite. Only the representative scans of each of the three clusters required phase identification, instead of performing 17 phase identifications.
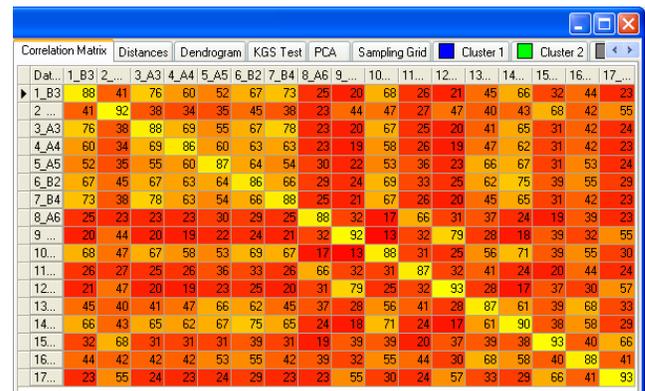


**Figure 4:** The correlation matrix, generated by comparing each dataset with each other.
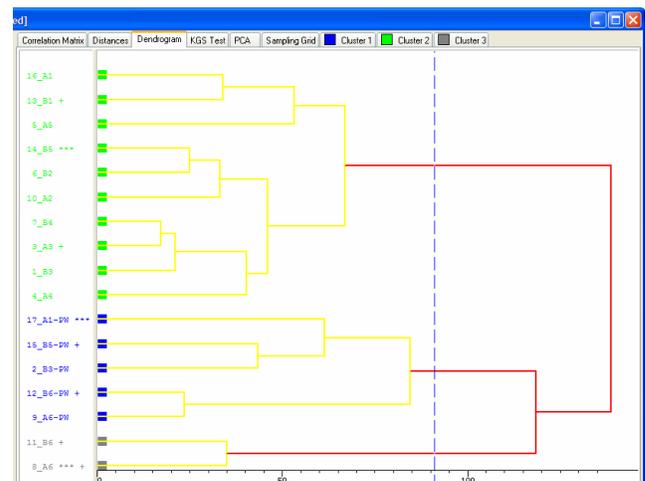


**Figure 5:** The dendrogram is a graphical display of the result of an agglomerative hierarchical cluster analysis (actual cut-off indicated by a blue stippled line).
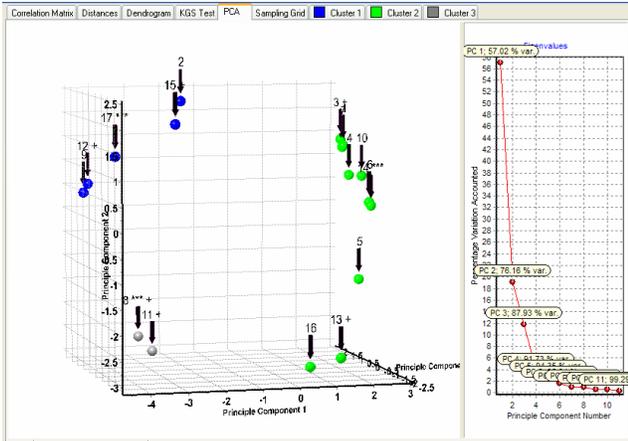
**Figure 6:** The PCA score plot (left) shows the clear separation of the datasets into 3 clusters; the first 3 shown principal components cover 88 percent of the variation in the data.
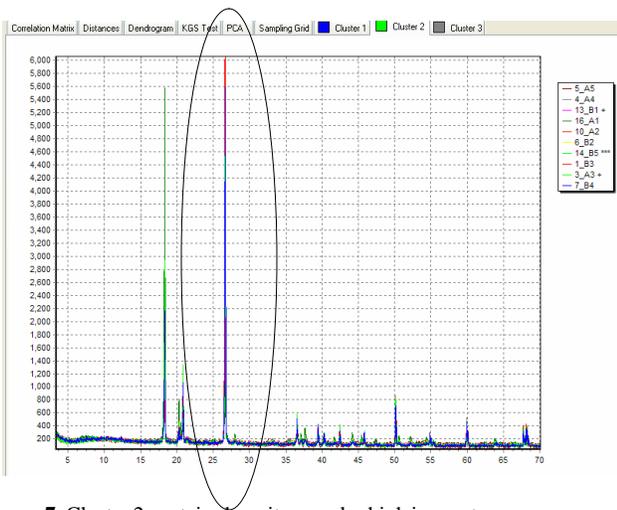


**Figure 7:** Cluster 2 contains bauxite samples high in quartz.

### Case Study 3: Rietveld analysis of hexagonal vs. monoclinic pyrrhotite ratios

Pyrrhotite (Po) is a name used to denote a *family* of Fe-deficient sulfides with the general formula, $Fe_{1-x}S$. Po is a ubiquitous mineral in sulfide deposits, most notably in those referred to as *magmatic sulfide deposits* (e.g. Sudbury, Ontario Canada). Most of these deposits are dominated by monoclinic pyrrhotite (mpo), presumably forming through the conversion from the hexagonal form (hpo). Hpo appears to be always present, albeit in low concentrations. However, hpo can also dominate in certain circumstances. Determination of hpo:mpo ratios is important from several standpoints of ore beneficiation:

1. hpo is non-magnetic (antiferromagnetic) vs. mpo which is magnetic (ferrimagnetic), creating a magnetic separation issue;

2. hpo oxidizes more readily than does mpo, creating problems in flotation cells;
3. hpo is slightly richer in Ni than mpo (for Sudbury, 1 vs. 0.55 wt.% Ni) and can thus actually be considered an ore mineral.

Existing strategies for determining the hpo:mpo ratio include etchants or magnetic colloids applied to polished thin film sections with subsequent image analysis to determine a ratio. These techniques are time and labor intensive, and often inaccurate due to sampling size, grain orientation, and other reasons.

1. Obtain ore samples. Specimens over five levels (2400 › 4200 ft) were obtained from the 100 Ore body of the North mine (INCO). Selected as it is known to contain areas with a high concentration of hpo;
2. Samples crushed and *micronized* to a grain size of < 10 μm (to minimize microabsorption effects). Samples 1-2 g used per XRD data collection;
3. A Philips PW1820 automated diffractometer, equipped with a Co*K* avg tube (to minimize fluorescence) was used to collect XRD data. Ranges of $2\theta = 5\text{-}95°$ and scan speeds of 0.06 °2θ /sec were employed (data collections ~ 4.5 hrs).
4. Diffractograms analyzed for phase identification (up to 10 phases noted);
5. Experimental diffractograms processed using Rietveld software available in the X'Pert HighScore Plus (Panalytical) set of programs;
6. Multiple aliquots were run to test for precision of method;
7. PTS made from samples in the respective ore zones and in-house image-analysis techniques used for accuracy tests. Samples were also etched with 50% HI, then the hpo:mpo ratios determined using image-analysis;
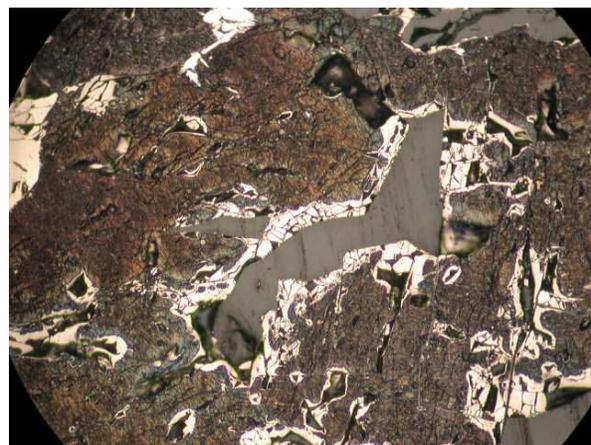8. Mineral chemistry obtained from etched samples for both hpo and mpo.



**Figure 8:** Etched Hexagonal Po with Monoclinic Po (white areas) at grain boundaries. North mine, 4200L. 20x mag.

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**Table 3: Rietveld refinement results for the samples from various depth levels.**

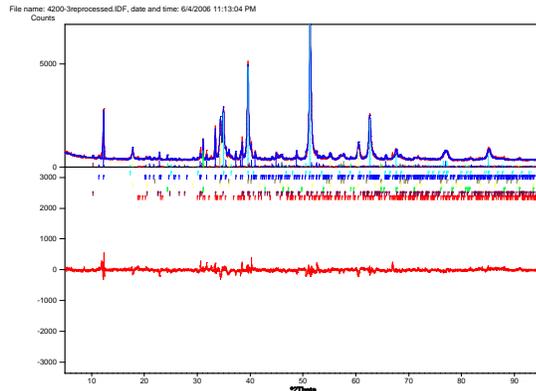| Mineral | Level | | | | |
|---|---|---|---|---|---|
| | **4200** | **4050** | **3880** | **3400** | **2400** |
| Hex po (Modal %) | 61.6 | 65.3 | 29.1 | 34.4 | 64.1 |
| Mono po | 2.2 | 2.1 | 4.1 | 1.5 | 14.1 |
| Pentlandite | 8.9 | 12.9 | 4.8 | trace | 9.0 |
| Chalcopyrite | 4.2 | n.d. | 4.1 | 19.3 | n.d. |
| Amphibole | 16.0 | 2.3 | 10.3 | 38.5 | 5.2 |
| Magnetite | n.d. | 3.9 | n.d. | n.d. | n.d. |
| Plagioclase | n.d. | trace | 27.8 | Not ref. | n.d. |
| Quartz | 3.5 | 6.9 | 11.1 | n.d. | trac |
| Biotite | 2.2 | 6.7 | 5.7 | 5.3 | 3.3 |
| Chlorite | n.d. | n.d. | n.d. | 1.1 | 4.0 |
| Hpo:mpo | 0.96 | 0.96 | 0.87 | 0.96 | 0.82 |



**Figure 9:** Rietveld refinement of sample 4200.

**Table 4: Results for 4200L Samples (Modal %).**

| Mineral | 4200-1 | 4200-2 | 4200-3 | Average | StdDev |
|---|---|---|---|---|---|
| Hex Po | 60.0 | 63.6 | 61.4 | 61.6 | 1.815 |
| Mono Po | 2.0 | 1.6 | 3.1 | 2.2 | 0.777 |
| Amph | 17.2 | 15.5 | 15.3 | 16.0 | 1.044 |
| Pent | 9.2 | 8.5 | 9.0 | 8.9 | 0.361 |
| Cpy | 3.8 | 4.6 | 4.1 | 4.2 | 0.404 |
| Qtz | 3.8 | 3.5 | 3.1 | 3.5 | 0.351 |
| Biot | 4.0 | 2.7 | 4.1 | 2.2 | 0.781 |

**Table 5:  Comparison of image analysis results to Rietveld.**

| | Image Analysis (w tape) | | | | | Difference |
|---|---|---|---|---|---|---|
| | 4200A | 4200B | 4200C | AVG | Rietveld | (%) |
| Opaque | 77.1 | 78.9 | 81.3 | 79.1 | 76.9 | 2.2 |
| Non Opaques | 22.9 | 21.1 | 18.7 | 20.9 | 24.1 | -3.2 |
| | | | | | | |
| Pyrrhotite | 68.7 | 79.5 | 84.4 | 77.5 | 83.0 | -5.5 |
| Pentlandite | 15.3 | 14.0 | 8.8 | 12.7 | 11.6 | 1.1 |
| Chalco | 16.0 | 6.5 | 6.9 | 9.8 | 5.4 | 4.4 |
| | | | | | | |
| Quartz | 21.7 | 38.6 | 37.1 | 32.5 | 17.6 | 14.9 |
| Amph | 78.3 | 61.4 | 62.9 | 67.5 | 82.4 | -14.9 |
| | | | | | | |
| Pyrrhotite | 53.0 | 62.7 | 68.6 | 61.4 | 61.6 | -0.2 |
| Pentlandite | 11.8 | 11.0 | 7.2 | 10.0 | 8.9 | 1.1 |
| Chalco | 12.3 | 5.1 | 5.6 | 7.7 | 4.3 | 3.5 |
| Quartz | 5.0 | 8.1 | 6.9 | 6.7 | 3.5 | 3.2 |
| Amph | 17.9 | 13.0 | 11.8 | 14.2 | 19.6 | -5.4 |

Rietveld refinements were carried out until the goodness of fit (GoF), was found to be <10%.

Results suggest significant variations in hpo:mpo ratios, possibly increasing with stratigraphic depth, and also illustrate the fact that the 100 ore body is indeed dominated by hpo.

To test the precision of the technique, one sample, 4200L, was selected and three independent data sets and Rietveld refinements made.

Etching and image analysis results were tabulated and compared to the Rietveld results.  Some similarities are seen, but some large variances are due to the shortcomings of the etching/image analysis technique.

**CONCLUSIONS**

Modern X-ray diffraction can provide valuable information for mining and exploration through standard less quantification and fast, statistical evaluation of large datasets through cluster analysis.  Today's optics, detectors, and software can provide rapid and accurate analyses suitable for process control environments as well as research.

**REFERENCES**

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