EFFICIENCY OF RIEtvELD-BASED XPD QUANTIFICATION OF MINERAL ABUNDANCE IN GRANITIC ROCKS, A CASE STUDY

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ABSTRACT

The structure-sensitive and standardless phase quantification method based on a Rietveld analysis of X-ray powder diffraction data was compared to some traditional techniques. It was found that the Rietveld-based method is at least equal, in several cases superior to the RIR technique, and can be a fast and simple substitute for the optical modal analysis. At the same time it is shown that the points of a Rietveld-based rock classification, using the QAP rock classification of Streckeisen, can be erroneously shifted on the diagram towards the higher plagioclase containing types due to the perthitic exsolution of K-feldspar and consequent inherent overestimation of the abundance of plagioclase.

Key words: Rietveld, XRD quantification, phase analysis, granitoid

INTRODUCTION

The basic goal of this study was to find an X-ray powder diffraction (XPD) phase quantification method that gets rid of the inherent restrictions and systematic errors of the classical internal standard based methods (e.g., RIR: Chung, 1974a, 1974b, 1975). Moreover, this XPD method should also offer an attractive alternative for the time consuming optical modal analysis as well as a reliable comparison based on the widely used mineral norms, calculated from bulk chemical analysis, (e.g., CIPW) for rock classification.

The Rietveld analysis has given the XPD method a new perspective providing a tool to extract classical structural as well as real-structural information from even fairly complex or multiphase powder patterns due to its characteristics like:

1) the applied profile function explicitly takes into account each peak of every phase of the sample making possible to handle (as well as reliably index the contributing single peaks) highly overlapping peak groups;
2) the difference diagram of the observed and calculated powder profile immediately indicates the presence of unaccounted for intensity contributions;
3) being basically a structure refinement method, the Rietveld analysis handles each and every mineral phase in its actual, individual structural state — that is this approach is structure-sensitive;
4) as every measurable hkl-group of each phase are included in the calculation, the effect of preferred orientation tends to be minimal.

As a kind of 'by-product', the refined scale factor of each constituting phase in the XPD profile of a powder mixture (e.g., minerals in a rock) is directly proportional to its relative abundance.

Several aspects of application of the Rietveld-based quantitative phase analysis for quantification of multicomponent standards and mineral mixtures were addressed by Bish et al. (1993). The present work concentrates on natural granitic rock samples, and aims a comparison of the Rietveld-based quantification results with two traditional rock analytical techniques, the optical modal measurement and the bulk chemical analysis-based norm calculations.

EXPERIMENTAL

In order to evaluate the efficiency of the Rietveld analysis as mineral quantification method for granitic rocks the following approaches were used:

1) quantification of the mineral composition of artificial mixtures modelling a wide range of granitic rock compositions by the traditional RIR method and Rietveld analysis;
2) applying the above methods to the quantification of an international standard granite sample ('GM' SZT SZEV 2290-80, red granite, Meissen, Germany, analyzed by 62 reference labs);
3) comparison of the results of the RIR and the Rietveld methods for quantification of the main mineral constituents of 'GM' granite by statistical analysis;
4) determination of the mineral composition of several granitoid rock samples from the Mórágy Hills belonging to the Fazekasboda-Mórágy Mts. region (Buda, 1995) by Rietveld analysis, optical modal measurement, and CIPW mesonorms (Parslow, 1969) calculated from the wet-chemical analyses of the whole rocks.

All the XPD measurements were carried out using side packed powder samples of 1 μm average grain size, on a Bragg-Brentano geometry Siemens D5000 theta-theta diffractometer equipped with a graphite secondary beam monochromator. The data collection was performed using CuKα (λ = 0.154178 nm) radiation scanning the 5–70° 2θ range by 0.02° 2θ stepsize and 5 s counting time/step.

The DBWS program package (Young and Sakhtivel, 1994) was used for Rietveld analysis, while the RIR values (Hubbard and Snyder, 1988) were individually determined on the same equipment. The optical modal values were determined on large thin sections by polarized light microscopy, while the CIPW norms were calculated using the MINPET program.
Semi-quantitative chemical analyses were carried out by means of an AMRAY 1830Ti/6 scanning electron microscope operated at 20 kV acceleration voltage using energy-dispersive X-ray spectrometry (EDAX® VP9800 ED) at the Department of Petrology and Geochemistry, ELTE.

Quantitative chemical analyses were performed using a JEOL JXA-733 electron microprobe analyser (EMP A) equipped with three wavelength-dispersive spectrometers (WDS), at the Geochemical Research Laboratory of the Hungarian Academy of Sciences. The measurements were carried out with: 15 kV accelerating voltage, 40 nA beam current, beam defocus 10 μm diameter, 32 x 4 s counting time. Analytical lines: Lα for Pb, Kα for Al, Ca, S, Cl and P, Kβ for As. The following standards were used: PbSe (synthetic) for Pb, artificial glass for Al, apatite for Ca, P and Cl, chalcopyrite for S, GaAs for As. For matrix correction conventional ZAF method was applied.

RESULTS AND DISCUSSION

The 'GM' standard granite sample was used for optimizing the refinement strategy and parameters of the Rietveld treatment. The best fit was achieved using a 5 parameter orthogonal polynomial fit for background treatment, the pseudo Voigt function for profile description, 5 FWHM region to handle the tail regions, March-Dollas function for preferred orientation correction, sample displacement correction and no correction for absorption, microextinction and surface roughness. Structural models for the main constituents (quartz, K-feldspar (low-microcline), plagioclase (low-albite), biotite (3T) and chlorite (clinochlor)) were taken from the ICSD database. The test mixtures were prepared using the following pure components: quartz - from the Velence Mts., (Hungary), microcline and albite - from Ytterby (Sweden), biotite - from Erdősmecské, Mecsek Mts., (Hungary). Rietveld refinement of each of these single phases (Fig. 1 shows refinement results for microcline ) indicated that:

1. No refinement of atomic positional parameters gives significantly better fit
2. Refinement of an overall isotropic thermal parameter ($B_{iso}$) is justified,
3. The traditional Rietveld formula describes properly the peak asymmetry down to $30^\circ$ 26 and a first order

Cagliotto formula gives suitable description of the angular dependence of the FWHM. 4. Cell parameters have to be included in the refinement.

The comparative study of the quantification of the artificial mixtures prepared and analyzed using the above-derived optimum experimental parameters, shed light on the following difficulties:

1) a heavy overlap of the strongest (that is the most desirable as analytical line) XPD reflections of the main rock forming minerals is very frequent;
2) the traditional intensity measurement is very much hindered by the uncertainty of the base line determination due to the even more heavily overlapping weak reflections;

3) all main mineral constituents, except quartz, are inclined to show preferred orientation of various degrees.

All these facts provide explanation why the Rietveld analysis was found to be superior to the RIR results in each case where one or more of the above phenomena occurred (the difference between the weight percentage derived by the above methods can be as high as 20%) (Fig. 2).

![Fig. 1. Rietveld analysis of the porphyroblastic microcline granitoid rock from Erdősmecské, Mecsek Mts., S-Hungary.](image)

![Fig. 2. Comparison of Rietveld and RIR/Chung phase quantification of the standard mixture #4.](image)

www.sci.u-szeged.hu/asvanytan/acta.htm
The mineral-by-mineral comparison and its statistical analysis in case of the ‘GM’ sample even more explicitly pointed out how sensitively the RIR method reacts to the unavoidable preferred orientation, while the Rietveld analysis was considerably affected only at the extremely high concentrations. The Rietveld analysis gave a slightly better fit even in the case of quartz showing that it can adapt to the slightest deviations from the structural model.

In the case of the natural granitoid samples not only the results of the two main XPD methods were compared, but also their output was corroborated with the results of their optical modal analysis as well as with the calculated CIPW norms of the same samples. There are slight differences in the comparison results between localities (Erdősmecsek, Kismórágy, Mórágy quarry), some main trends, however, can still be recognized:

1) the Rietveld analysis results approximate the optical modal values significantly better than the RIR results do;
2) the greatest discrepancies were found in the case of biotite. It is obviously due to its extremely severe preferred orientation (that is to the fact that one method can handle this phenomenon by modeling, while the others can not);
3) in all cases the XPD quantification results fit better the mesonorm values than the optical modals.

The accuracy of the optical modal analysis depend heavily on the grain size (as well as on the number of measurements), consequently large megacrysts are fairly difficult to handle. Accordingly the resulting modal values are more representative to the small-grained rock fraction (‘base material’). The mesonorm calculations are based on bulk wet-chemical analysis; consequently it is independent of the grain-size of the rock. Since the XPD measurements are also carried out on powdered rock samples, their better fit with the corresponding mesonorms is expected (Fig. 3A, B, C, D).

A comparison of rock classification based on the QAP rock classification diagram of Streckeisen (1974) was performed using phase abundance values obtained by three different methods (Rietveld, optical modal, and CIPW mesonorms) (Fig. 4). Comparing the Rietveld based

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**Table 1:** Phase abundance values obtained by different methods for Erdősmecsek and Kismórágy.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Erdősmecsek</th>
<th>Kismórágy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>23.4%</td>
<td>24.8%</td>
</tr>
<tr>
<td>K-Feldspar</td>
<td>24.0%</td>
<td>16.4%</td>
</tr>
<tr>
<td>Plagioclase</td>
<td>35.3%</td>
<td>37.3%</td>
</tr>
<tr>
<td>Biotite</td>
<td>16.0%</td>
<td>21.1%</td>
</tr>
<tr>
<td>Conundrum</td>
<td>1.3%</td>
<td>1.4%</td>
</tr>
<tr>
<td>Σ</td>
<td>100.0%</td>
<td>100.0%</td>
</tr>
</tbody>
</table>

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**Fig. 3A.** Comparison of phase quantification of the granitoid from Erdősmecsek, Mecsek Mts., S-Hungary, by different methods.

**Fig. 3B.** Comparison of phase quantification of the granitoid from Kismórágy, Mecsek Mts., S-Hungary, by different methods.
Fig. 3A. Comparison of phase quantification of the granitoid from Mórágy quarry, Mecsek Mts., S-Hungary, by different methods.

classification with those, derived from CIPW catalog norms calculations (Buda, 1995) it was found that the Rietveld-based compositions tend to indicate higher quartz and plagioclase containing rock types (granodiorite).

**CONCLUSIONS**

The Rietveld-based XPD phase quantification method proved to be an efficient tool to determine the mineral abundance in granitic rocks. Its most desirable feature is the structure sensitivity. It means that it takes into account the actual structural state of the constituting minerals as compared to the external standardization inevitable in the RIR method. The comparative measurements on artificial mineral mixtures (modeling a wide range of granitic compositions), on natural samples (granites from the Mecsek Mts.), as well as on the international granite rock standard 'GM', proved the superiority of the title method over the RIR technique. It is mainly due to its capability of handling heavily overlapping peak groups as well as its efficiency in the treatment of the effect of preferred orientation.

Comparing the Rietveld results to the optical modal measurements and calculated CIPW norms of the same natural samples it was found that the Rietveld-based XPD method is a suitable replacement of the time consuming optical modal analysis. The comparison with the CIPW mesonorms, however, pointed out the need of cautious treatment of porphyric constituents in grain size dependent methods like the later.

The comparison of Rietveld-based rock classification with those of modal-based ones pointed out an inherent feature of the Rietveld quantification; no distinction can be made between a self-contained and a perthitic albite phase. Accordingly the Rietveld-derived plagioclase content is higher than the amount of the modal plagioclase. Consequently the Rietveld-based rock classification is erroneously shifted towards the plagioclase-rich rock types. The conclusions of this study are in good accordance
Fig. 4. Rock classification by Streckeisen’s QAP discriminative range of rock types. Their finding concerning the superiority of using capillary packed sample, that is a transmission type Rudnánszky for the precious grain size, magnetic, and diagram based on phase abundances obtained by different quantification methods.

with the results published by Hill et al. (1993) for a wider range of rock types. Their finding concerning the superiority of using capillary packed sample, that is a transmission type data collection, over the reflection-type one reassures the expectation of the authors that changing the diffraction geometry from Bragg-Brentano to Debye-Scherrer would further improve the results by eliminating the preferred orientation phenomenon.

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