

Quantitative mineralogical analysis using the Rietveld full-pattern fitting method

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ABSTRACT

Quantitative phase analysis of a number of multicomponent standard and natural mineral mixtures has been done using an adaptation of the Rietveld method. Binary mixtures (most 50:50 by weight) of corundum with quartz, hematite, ilmenite, magnetite, biotite, analcime, mordenite, or clinoptilolite were analyzed, using digital powder X-ray diffraction (XRD) data. In addition, a suite of standard mixtures of hematite and corundum, a natural feldspar mixture, the G-1 standard granite, two natural bauxite samples, and a mixture of biogenic carbonate minerals were also analyzed. Quantitative information was extracted from refined individual scale factors and unit-cell volumes (derived from refined unit-cell parameters), obtained with a Rietveld refinement program modified to analyze up to ten phases. The quantitative results for standard mixtures were within 2.5% (absolute) of the true values, with the exception of the hematite, ilmenite, and magnetite mixtures. Results for the latter mixtures using $\text{CuK}\alpha$ data were severely affected by microabsorption, but analysis of the hematite mixtures using $\text{FeK}\alpha$ radiation gave results with absolute errors $\leq 2\%$. Results for the G-1 granite and the natural feldspar agreed well with optically determined modes, and the method facilitated separation of the significant overlaps in the pattern of the carbonate minerals.

Quantitative mineralogical analysis by the Rietveld method has several significant advantages over conventional methods of quantitative analysis. The method uses all intensity data in a pattern rather than a few of the most intense reflections, partially compensating for preferred orientation and extinction. In addition, standard data are calculated for each phase during analysis, overcoming the troublesome requirement of obtaining standards representative of the materials in an unknown. It is also possible to gain a wealth of information from each sample in addition to amounts of phases. Because some of the most troublesome systematic errors, including sample displacement and zero-point shift, can be refined, the method yields unit-cell parameters of an accuracy comparable with that obtained when using an internal d -value standard. The method should find a wide application in geology, including in modal analysis and compositional determinations of individual mineral components using unit-cell parameter systematics.

INTRODUCTION

X-ray powder diffraction has been a popular method of quantitative mineralogical analysis for over 40 yr. The power and convenience of the method lie in its simplicity and speed and in the fact that the method can be applied to a wide range of materials. It is especially useful for fine-grained sedimentary or volcanic rocks that are not amenable to quantitative study by optical methods. The importance of the powder diffraction method to quantitative analysis is illustrated by the large number of papers on many different classes of materials (e.g., Brindley, 1980; Snyder and Bish, 1989). However, in spite of the large amount of routine work in the area of quantitative X-ray powder diffraction analysis, the method still largely remains semiquantitative except in special cases. Numerous instrumental and sample-related problems must be

addressed in order to obtain accurate results; these include particle statistics, primary and secondary extinction, microabsorption, preferred orientation, separation of overlapping and broad reflections, variation in standard data with composition, availability of pure standards, and detection of amorphous and trace phases (Klug and Alexander, 1974; Bish and Chipera, 1988). In addition, traditional methods require that standard data be acquired for every phase present in the mixtures to be analyzed.

The Rietveld method of quantitative analysis minimizes or eliminates many of these problems (Bish and Howard, 1986, 1988; Hill and Howard, 1987; Snyder and Bish, 1989). Rietveld refinement was originally developed as a method of refining crystal structures using powder neutron diffraction data (Rietveld, 1969), and the application of the method to mineralogy was summarized

by Post and Bish (1989). Refinement is done by minimizing the sum of the weighted, squared differences between observed and calculated intensities at every 2θ step in a digital powder diffraction pattern. Thus, refinement is done on a point-by-point basis rather than on a reflection basis. The calculated intensity at a given step (y_{ic}) is determined by summing the contributions from background and all neighboring Bragg reflections (k) for all phases (p) as

$$y_{ic} = \sum_p S_p \sum_k p_k L_k |F_k|^2 G(\Delta\theta_{ik}) P_k + y_{ib}(c) \quad (1)$$

where S is the scale factor, L_k is the Lorentz and polarization factors for the k th Bragg reflection, F_k is the structure factor, p_k is the multiplicity factor, P_k is the preferred orientation function, θ_{ik} is the Bragg angle for the k th reflection, $G(\Delta\theta_{ik})$ is the reflection profile function, and $y_{ib}(c)$ is the refined background (Wiles and Young, 1981). The parameter most often used to assess the fit is R_{wp} , the weighted profile residual, and

$$R_{wp} = [\sum w_i (y_{io} - y_{ic})^2 / \sum w_i y_{io}^2]^{0.5} \quad (2)$$

where y_{io} and y_{ic} are the observed and calculated intensities, respectively, at point i in a diffraction pattern and w_i is the weight assigned to each intensity. For a perfect refinement, the final R_{wp} would equal R_{exp} , and

$$R_{exp} = [(N - P) / \sum w_i y_{io}^2]^{0.5} \quad (3)$$

where N is the number of data points in the pattern, and P is the number of parameters refined. Typical values of R_{wp} range from a few percent for very good neutron refinements to 20–30% for X-ray refinements, depending in part on the count times used, the degree of preferred orientation, and the number of variable parameters.

Quantitative analysis by the Rietveld method requires a knowledge of the approximate crystal structure of all phases of interest (not necessarily all phases present) in a mixture. The input data to a refinement include space group symmetry, atomic positions, site occupancies, and unit-cell parameters. In a typical Rietveld quantitative analysis, individual scale factors (related to the amounts of each phase) and peak-shape parameters for each phase are varied along with background and unit-cell parameters. Atomic positions and site occupancies can also often be successfully varied for major phases if such detailed information is of interest, although in some cases (e.g., zeolites), site occupancies of some sites must be varied to obtain accurate scale factors. Information on the weight fractions (W_i) of phases present in a mixture is calculated from the scale factors for each phase obtained from the refinement

$$W_i = S_i \rho_i V_i^2 / \sum_j S_j \rho_j V_j^2 \quad (4)$$

where S_i , ρ_i , and V_i are the scale factor, density, and unit-cell volume, respectively, of phase i , and the summation is over all phases present.

Few applications of Rietveld quantitative analyses have been published, particularly for geological samples, although the strength and versatility of the method suggest that it should be a powerful tool for analyzing geologic samples. Among others, Hill and Howard (1987), Bish and Chipera (1988), Bish and Howard (1988), Bish and Post (1988), and Reid et al. (1992) presented examples of quantitative analysis of a variety of mixtures, and we have successfully applied the method to mineral mixtures containing up to ten components.

The Rietveld method of analysis provides numerous advantages over conventional quantitative analysis methods. As the method uses a whole pattern-fitting algorithm, all lines for each phase are explicitly considered, and even severely overlapped lines are usually not a problem. Thus it is not necessary to decompose patterns into separate Bragg peaks, as is often the case for traditional methods. The use of all reflections in a pattern rather than just the strongest ones minimizes both the uncertainty in the derived weight fractions and the effects of preferred orientation, primary extinction, and nonlinear detection systems. Also, failure to consider a phase in the analysis will yield obvious differences between the observed and calculated diffraction patterns and reveal unsuspected minor phases. Along with a quantitative analysis, it is also possible to refine structural parameters, including atom positions, site occupancies, and unit-cell parameters for each phase in the mixture. One attractive feature of this method is that it is possible to calculate tailor-made standards to match the phases in a given mixture, e.g., the composition, unit-cell parameters, or extent of order-disorder in solid-solution phases can be refined to match the unknown as closely as possible. The method is not standardless, however, as it uses calculated standard data.

Preferred orientation of crystallites is one of the most serious problems inherent in conventional quantitative analyses, and numerous sample preparation methods have been proposed to minimize or to eliminate the problem. However, because the Rietveld method uses all classes of reflections, the effects of preferred orientation on quantitative analyses (scale factors) are greatly minimized. Orientation effects on unit-cell parameters are also minimal, but they can significantly affect site occupancies and atomic positions. The Rietveld method presents the opportunity to correct for preferred orientation using the March function (Dollase, 1986) or symmetrized harmonics (Jarvinen, 1992). Although older preferred orientation correction methods do not work well with quantitative analysis, the March function works better as it is normalized to the unit integral, and a change in its value will not affect the scale factors (e.g., Hill and Howard, 1987).

In this paper, we describe the application of the Rietveld method of quantitative analysis to a variety of geologically significant systems. These applications show the power and versatility of this method and show the types of information, in addition to amounts of phases, that can be obtained in a Rietveld quantitative analysis.

EXPERIMENTAL METHODS

Samples

Numerous standard mixtures were prepared to assess the precision and accuracy of the Rietveld quantitative analysis method. Binary mixtures (50:50 by weight) were prepared by mixing 1.0- μm metallurgical-grade corundum with the given mineral (Table 1). In addition to the laboratory-prepared mixtures of minerals, several natural samples were examined, including a feldspar separate ($\rho = 2.51\text{--}2.60\text{ g/cm}^3$) from a rhyolite lava near the Timber Mountain caldera complex adjacent to the Nevada Test Site, Nevada, and a mixture of coralline algae and echinoid spines containing aragonite and two compositionally distinct calcites. As a test of the method on complex geologic mixtures, the U.S. Geological Survey standard granite G-1 (Chayes, 1951) was examined. Finally, several natural bauxite samples were analyzed to assess the ability of the method to accommodate samples containing poorly crystalline minerals and minerals with a wide range of peak widths.

Data measurement

X-ray diffraction data for this study were obtained on Siemens D-500 and Scintag PAD V automated diffractometers, both with incident- and diffracted-beam Soller slits. The Siemens instrument used either a diffracted-beam graphite monochromator with a scintillation detector or a Kevex Psi solid-state Si (Li) detector, and the Scintag diffractometer used a solid-state intrinsic-Ge detector. Conventional data measurement parameters were used in these analyses, usually scanning from 2 to 70° 2θ and counting for 2.0 s every 0.02 or 0.03° 2θ . Most analyses used $\text{CuK}\alpha$ radiation, but $\text{FeK}\alpha$ radiation was used with some of the hematite-corundum mixtures, and a Hawaiian sample of bauxite was measured with $\text{CoK}\alpha$ radiation. Prior to analysis, all samples were milled under acetone to a mean particle size of <3 μm using a Brinkmann Micro Rapid mill. Particle size distributions were verified using a Horiba centrifugal particle size analyzer calibrated using Duke Scientific glass microanalysis spheres. Powders were mounted in a variety of ways, including front- and back-packed cavities, smear mounts, and glass-fiber mounts, to allow assessment of the effects of sample preparation on quantitative results.

Rietveld refinement

All Rietveld quantitative analyses reported here used a significantly modified version of the program DBW3.2 (Wiles and Young, 1981; Bish and Howard, 1988). The DBW program has been adapted to perform both internal- and external-standard analyses and can thus be used to determine the amount of noncrystalline materials present in a mixture. These two modifications are analogous to the matrix-flushing and adiabatic methods, respectively, of Chung (1974a, 1974b). The internal-standard method involves the addition to a sample of a known amount of a crystalline substance, usually corundum in our anal-

TABLE 1. Rietveld quantitative analysis results for various binary mineral mixtures*

Mineral	Source	Known wt%	Refined wt%
Quartz	Hot Springs, Arkansas	50	49.9(3)**
Corundum		50	50.1(5)
Analcime	Wikieup, Arizona	50	48.2(5)
Corundum		50	51.8(7)
Clinoptilolite	Nevada Test Site (NTS)	50	50.1(7)
Corundum		50	49.9(7)
Clinoptilolite	Castle Creek, Idaho	50	52.7(9)
Corundum		50	47.3(5)
Mordenite	Union Pass, Arizona	50	48.8(1.7)
Corundum		50	51.2(4)
Biotite	Bancroft, Ontario	50	47.5(3.0)
Corundum		50	52.5(7)
Ilmenite	Koidu, Sierra Leone	50	25.7(3)
Corundum		50	74.3(1.2)
Magnetite	Espanola, Ontario	50	38.1(2)
Corundum		50	61.9(4)

* $\text{CuK}\alpha$ radiation.

** Values in parentheses represent estimated standard deviations in the last quoted place.

yses. The external-standard method imposes the constraint that the sum of all phases determined in the mixture total to 100%. Thus the presence of amorphous phases or crystalline materials not explicitly included in the analyses will give incorrect absolute but correct relative analyses. These methods of analysis differ significantly from that used by O'Connor and Raven (1988), in which they determined the constant parameters in Equation 1 from measurements of a single sample. In light of their results on a 50:50 quartz to corundum mixture, in which they concluded that their quartz contained 18% amorphous component, it appears that some pitfalls may exist with this approach. A further difference in our implementation of the Rietveld quantitative analysis method involves the treatment of the unit-cell volume. Because the volume can be precisely determined during Rietveld refinement from the unit-cell parameters, we have included the cell volume with the variable, phase-specific parameters in the refinement. Other authors have retained the cell volume with other constant and phase-specific parameters in the scale factor (Hill and Howard, 1987; O'Connor and Raven, 1988).

Analyses were typically conducted on either an IBM 4381 or a DEC MicroVAX III computer, although the program has been modified to run on a personal computer. In most cases, refinement involved the sequential variation of scale factor for each phase, background coefficients, unit-cell parameters for each phase, specimen-displacement correction, peak-width parameters for each phase, and Pearson VII or pseudo-Voigt profile function coefficients for each phase in the mixture. It is important to note that the use of a single, simple profile function for each phase in a mixture will not allow accurate modeling of observed profiles resulting from highly anisotropic crystallite size and strain effects. Apart from applications to very fine-grained or disordered materials such as soils, this shortcoming should not present a significant

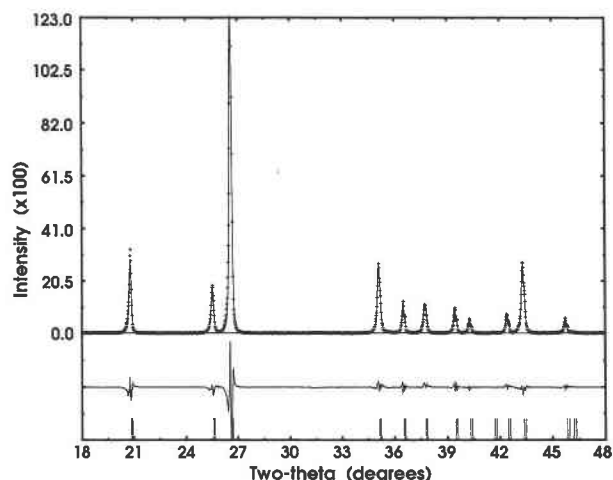


Fig. 1. Observed (pluses) and calculated (line) diffraction patterns for a 50:50 quartz-corundum mixture ($R_{wp} = 18.4\%$, $R_{exp} = 6.7\%$). The relatively straight curve near the bottom of observed and calculated data is the refined background. The lower curve shows the difference between observed and calculated patterns. Vertical marks at the bottom indicate the positions of allowed $K\alpha_1$ and $K\alpha_2$ reflections.

problem. During the course of refinement, atomic coordinates, occupancies, and temperature factors for each phase were usually fixed. However, in some cases, atomic coordinates and site occupancies were refined to determine additional structural information on the individual phases in mixtures. Starting atomic structural parameters were taken from the literature. The original Rietveld preferred-orientation correction in our version of DBW was not refined, as preliminary tests with the correction showed that quantitative analytical results were invariably better when preferred orientation was ignored.

RESULTS AND DISCUSSION

Quantitative analysis results for the binary mixtures are summarized in Table 1, and a discussion of each mixture follows. Estimated standard deviations for each value in Table 1 were derived from the estimated standard deviations on individual scale factors for the respective phases, and other error contributions were not included. The 50:50 quartz-corundum mixture gave a mineralogical composition statistically identical to the known composition, as well as unit-cell parameters of high precision and accuracy (Table 2). Because the Rietveld method attempts to fit every data point in a pattern rather than dealing with individual peak positions, and because complex and overlapping patterns are explicitly fitted with the method, unit-cell parameters obtained by Rietveld refinement are generally superior to those obtained by more conventional powder or single-crystal methods. Thus, the Rietveld method usually yields high-precision unit-cell parameters, and, if sample displacement and transparency corrections are refined, the values are also very accurate (Post and Bish, 1989). The observed and calculated patterns for the quartz-corundum mixture are shown in Figure 1. Most of the detail in the difference curve in Figure 1 is due to the inability of the profile function in the Rietveld program to fit the observed profiles accurately. Quantitative analysis results for this and most mixtures were relatively insensitive to variations in profile parameters and overall temperature factors, and the quantitative results usually changed little after refinement of unit-cell parameters, when the starting values for unit-cell parameters were nearly correct. Refinement of site occupancies is required only with minerals of complex composition or extensive solid solution. For example, analysis of a mixture containing an intermediate olivine sample of unknown composition would benefit from refinement of the olivine divalent cation site occupancies to determine both the approximate composition of the

TABLE 2. Unit-cell parameters obtained from the refinement of binary mixtures

	a (Å)	b (Å)	c (Å)	β (°)
Quartz	4.9110(1)		5.4021(4)	
Will et al. (1988)	4.91239(4)		5.40385(7)	
Corundum	4.7565(1)		12.984(1)	
Thompson et al. (1987)	4.7586(1)		12.9897(1)	
Analcime	13.6732(4)		13.696(1)	
Clinoptilolite (Idaho)	17.682(2)	17.974(2)	7.4158(8)	116.195(8)
Clinoptilolite (NTS)	17.6375(1)	17.9622(5)	7.4000(1)	116.220(1)
Mordenite	18.108(5)	20.451(5)	7.514(2)	
Biotite	5.349(2)	9.248(3)	10.208(1)	100.25(3)
Hematite				
Natural, $FeK\alpha$	5.03481(2)		13.7493(3)	
Kastalsky and Westcott (1968)	5.0340(7)		13.752(3)	
Ilmenite	5.06463(5)		13.9228(7)	
Wechsler and Prewitt (1984)	5.0884(1)		14.0855(4)	
Magnetite	8.39293(8)			
Hill et al. (1979)	8.394			

Note: literature values of unit-cell parameters are compared with Rietveld values to demonstrate the apparent accuracy of the Rietveld results. It is not expected, however, that the two results should be identical, as the samples (and methods) differ for most materials. In particular, routine single-crystal X-ray diffraction measurements do not necessarily yield highly accurate unit-cell parameters.

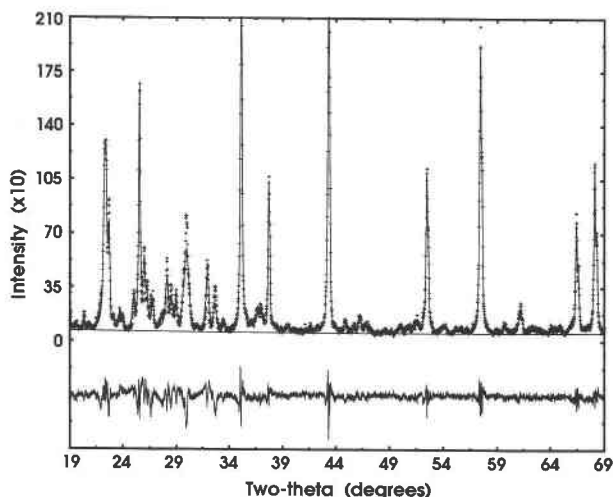


Fig. 2. Observed and calculated patterns for the 50:50 mixture of clinoptilolite (NTS) and corundum (conventions as in Fig. 1; $R_{wp} = 14.7\%$, $R_{exp} = 7.5\%$).

olivine and the extent of any intracrystalline cation ordering, and as a result the calculated olivine standard pattern would be a near perfect match to the observed pattern.

Analysis of the 50:50 analcime-corundum mixture also gave accurate quantitative results (Table 1), and the refinement resulted in significantly noncubic unit-cell parameters for analcime (Table 2). Although analcime has traditionally been considered to be cubic, Mazzi and Galli (1978) showed that most analcime deviates slightly from cubic symmetry because of Al-Si ordering. It is noteworthy that analcime could be stably refined assuming tetragonal symmetry, and the final a and c unit-cell parameters differ by more than 20σ . Comparison of the refined unit-cell parameters for this analcime with data given by Mazzi and Galli (1978) suggests that this sample is silica rich, typical of sedimentary analcime.

The 50:50 clinoptilolite-corundum mixture illustrates one of the most significant advantages of the Rietveld method in analyzing complex mixtures of minerals, the ability to explicitly accommodate severely overlapping reflections. The observed and calculated diffraction patterns for this mixture (Fig. 2) show the very large number of reflections (>300) used in the analysis. Figure 3 is an expansion of the region between 21.0 and $25.0^\circ 2\theta$, illustrating the significant peak overlap in this region. The most intense doublet in this region is composed of six independent reflections, a situation that would make indexing this pattern difficult even when applying techniques such as profile refinement, in which overlapping reflections are decomposed without relation to a structural model (Howard and Preston, 1989). Such a severe overlap would make unit-cell refinement by conventional methods very difficult, but the Rietveld method routinely gave very precise parameters (Table 2) in addition to excellent quantitative results. It is difficult to assess unit-

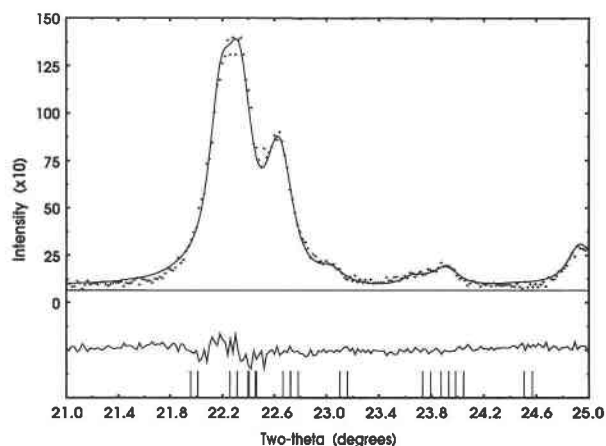


Fig. 3. Expansion of the 21.0 – 25.0° region of Fig. 2.

cell parameter accuracy for materials such as clinoptilolite (and analcime, mordenite, and biotite) because of compositional variabilities from sample to sample, although results for well-characterized materials suggest that the refined parameters for these phases are also accurate.

Mordenite is one of the more difficult minerals to deal with in quantitative analysis of zeolitic tuffs, primarily because of its variable exchangeable-cation composition, fibrous morphology with consequent high degree of preferred orientation, and peak overlap with coexisting phases such as clinoptilolite. In contrast to conventional methods, which yield results of variable quality (e.g., Bish and Chipera, 1989), the Rietveld method consistently gave good results on the mordenite standard mixtures studied (Table 1). Figure 4 shows observed and calculated patterns for the corundum–Union Pass mordenite mixture, and the refined mordenite unit-cell parameters obtained in this refinement are given in Table 2. The data in Figure 4 illustrate the ability of the method to accentuate phases that are unaccounted for in the model; note the discrepancy between observed and calculated patterns in the vicinity of $22.0^\circ 2\theta$ due to the presence of a small amount of opal-CT in the mordenite standard.

The 50:50 biotite-corundum mixture serves as an example to assess the effects of preferred orientation on Rietveld quantitative analyses. The observed and calculated data (Fig. 5) show a poor fit because of preferred orientation; the preferred-orientation correction was not varied in these refinements. In spite of the poor fit and the large amount of preferred orientation, quantitative results were reasonably good (Table 1). Cell parameters obtained for biotite are given in Table 2. This analysis highlights one of the strengths of the Rietveld method as compared with traditional methods that rely upon ratios of only a few reflections. Apparently, the effects of preferred orientation are somewhat moderated by the use of all reflections in a given pattern. Some observed reflections will be too intense and others will be too weak, but the overall least-squares refinement yields good quanti-

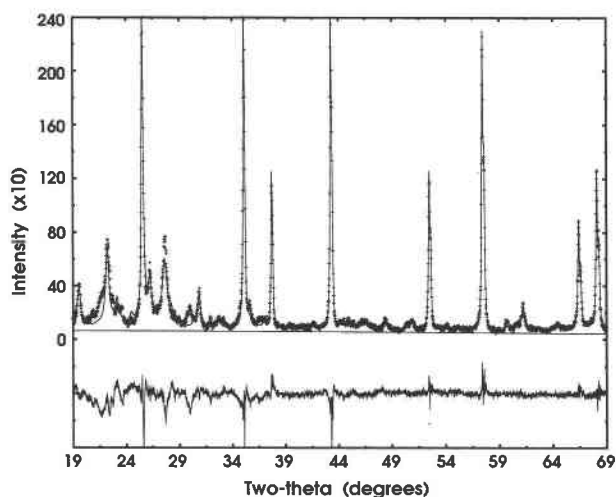


Fig. 4. Observed and calculated patterns for a 50:50 mordenite-corundum mixture (conventions as in Fig. 1; $R_{wp} = 16.8\%$, $R_{exp} = 7.1\%$).

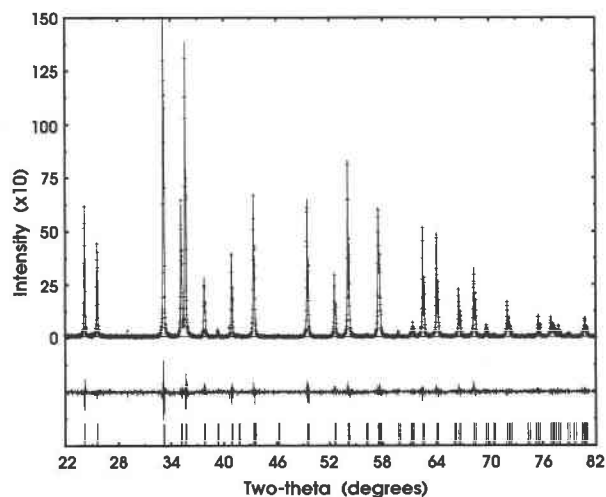


Fig. 6. Observed and calculated patterns for a 50:50 hematite-corundum mixture (conventions as in Fig. 1; $R_{wp} = 21.4\%$, $R_{exp} = 18.4\%$).

tative results. However, attempting to refine structural parameters could be disastrous; only scale and unit-cell parameters apparently remain largely unaffected.

The mixtures of hematite and corundum illustrate one of the most serious potential problems with the Rietveld method when analyzing mixtures with one or more phases having a linear absorption coefficient significantly greater than the average for the sample. In spite of the good agreement between observed and calculated patterns for the 50:50 mixture of synthetic hematite and corundum measured with $CuK\alpha$ radiation (Fig. 6), the quantitative results, 44% hematite and 56% corundum (Table 3), were relatively poor. As emphasized by Bish and Howard (1988), the poor results for this sample are probably due to microabsorption, yielding low relative weight percents

for the highly absorbing material, hematite ($\mu/\rho = 219 \text{ cm}^{-1}$ compared with 31 cm^{-1} for corundum). This problem can be minimized by grinding samples to very fine particle sizes or choosing a different radiation. However, extreme grinding should be avoided, as it can eventually cause degradation of the diffraction pattern. Refinements with data obtained on <400 mesh material (<38 μm instead of <3 μm) yielded even worse results (20:80 hematite to corundum for a 50:50 mixture), consistent with the effects of microabsorption. Analysis of the mixtures using $FeK\alpha$ radiation data virtually eliminated the microabsorption problem, yielding 50% hematite and 50% corundum for the 50:50 mixtures (hematite $\mu/\rho = 56$ compared with 62 cm^{-1} for corundum). Table 3 tabulates the results for a series of hematite-corundum mixtures analyzed with both $CuK\alpha$ and $FeK\alpha$ radiation. These mixtures are a good example of a case in which conventional methods will implicitly correct for the problem during standardization, therefore potentially yielding results superior to those obtained with the Rietveld meth-

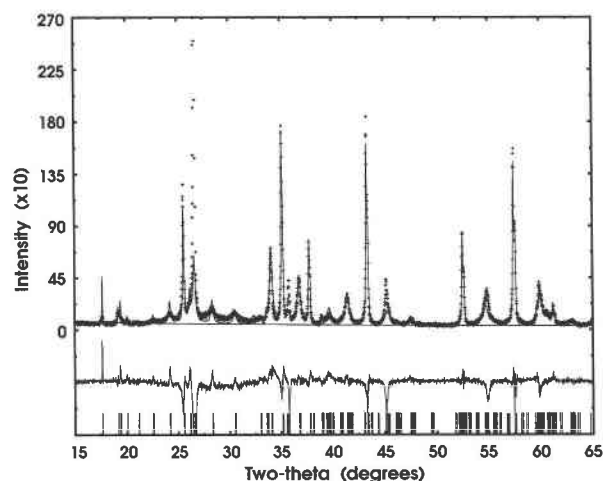


Fig. 5. Observed and calculated patterns for a 50:50 biotite-corundum mixture (conventions as in Fig. 1; $R_{wp} = 32.2\%$, $R_{exp} = 8.5\%$).

TABLE 3. Rietveld quantitative analysis results for various mixtures of hematite* and corundum using $CuK\alpha$ and $FeK\alpha$ radiation

Hematite to corundum	Radiation	
	$CuK\alpha$	$FeK\alpha$
20:80	16:84	19:81
40:60	34:66	39:61
50:50	44:56	50:50
50:50**	20:80	50:50
60:40	53:47	58:42
80:20	77:23	78:22
90:10	n.a.†	88:12

Note: results are in weight percent.

* Synthetic hematite unless otherwise specified.

** Cleator Moor, England.

† The abbreviation n.a. = not analyzed.

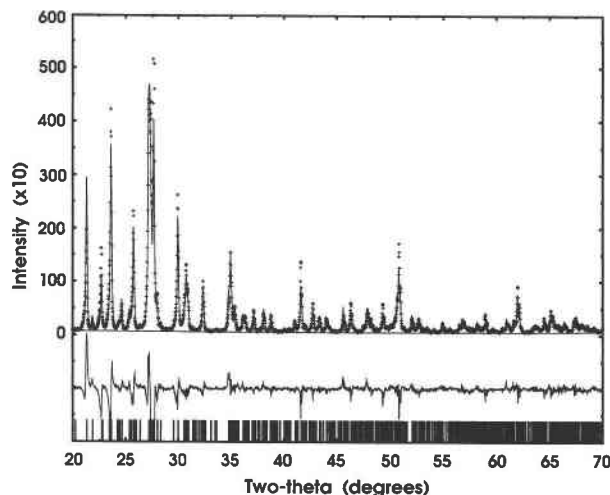


Fig. 7. Observed and calculated patterns for volcanic feldspars (conventions as in Fig. 1; $R_{wp} = 26.6\%$, $R_{exp} = 6.2\%$).

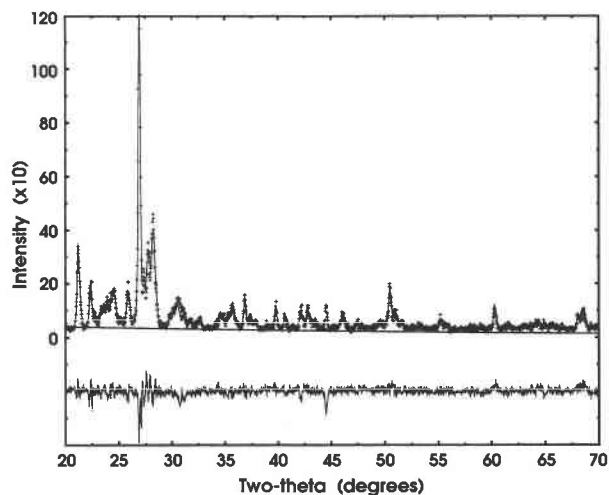


Fig. 8. Observed and calculated patterns for the G-1 standard granite (conventions as in Fig. 1).

od, if microabsorption effects are not considered in the analysis. In spite of the microabsorption problem, precise and accurate cell parameters were still obtained with $CuK\alpha$ radiation (Table 2). The microabsorption problem is most severe when the high linear absorption coefficient material is a minor component of the mixture, i.e., when μ/ρ for phase α is very different from the average μ/ρ of the mixture. However, for typical rock mixtures containing a small amount, e.g., a few percent, of an Fe-bearing phase, the errors due to microabsorption will probably not be the limiting factor in the accuracy of the analysis. For small amounts of a phase, the error in the refined scale factor will typically be comparable with that due to microabsorption, and quantitative results will not have large absolute errors. As pointed out by Bish and Howard (1988), the Rietveld method provides an opportunity to calculate the linear absorption coefficient for every phase in a mixture, thereby facilitating a correction for microabsorption problems if an average crystallite shape and size are assumed (see Klug and Alexander, 1974, p. 541–542). Taylor and Matulis (1991) recently presented results of a simple correction for microabsorption during Rietveld quantitative analysis that appears to work reasonably well for a mixture of LiF ($\mu/\rho = 20 \text{ cm}^{-1}$) and $Pb(NO_3)_2$ ($\mu/\rho = 231 \text{ cm}^{-1}$, $CoK\alpha$ radiation). The good results obtained with finely ground hematite-corundum mixtures using $FeK\alpha$ radiation illustrate that the Rietveld method of quantitative analysis can be applied even to mixtures containing large amounts of Fe-bearing phases through judicious selection of radiation and proper sample grinding.

Results for the ilmenite-corundum and magnetite-corundum mixtures were similarly affected by microabsorption. Both 50:50 mixtures yielded poor quantitative results with $CuK\alpha$ radiation (Table 1), but precise and apparently accurate unit-cell parameters were obtained (Table 2). The differences between the two sets of ilmenite

unit-cell parameters in Table 2 are probably due to variations in composition. These results are comparable with the results for the natural hematite and corundum mixtures with $CuK\alpha$ radiation. The ilmenite-corundum and magnetite-corundum mixtures were not analyzed with $FeK\alpha$ radiation.

Natural geologic samples are more difficult to use to demonstrate the accuracy of the Rietveld method of quantitative analysis because of the lack of well-characterized materials for test standards. Figure 7 shows the observed and calculated patterns for the mixture of two volcanic feldspars separated from a tuff; the fit is good, considering the complexity of the pattern, the large number of reflections, and the presence of significant preferred orientation. Rietveld quantitative analysis yielded 93% sanidine and 7% high albite, agreeing well with the independent point count results (100 grains, D. Broxton) of 93% sanidine and 7% albite. Cell parameters for sanidine were $a = 8.4499(4)$, $b = 13.008(1)$, $c = 7.1755(4)$ Å, and $\beta = 116.069(5)^\circ$; parameters for high albite were $a = 8.211(3)$, $b = 12.926(6)$, $c = 7.128(2)$ Å, $\alpha = 93.35(5)$, $\beta = 116.37(3)$, and $\gamma = 90.15(4)^\circ$. The cell parameters determined from this analysis can be used with the familiar b - c plots (e.g., Stewart and Wright, 1974) to determine composition and the state of ordering of the feldspars. Use of the b - c plot with these cell parameters shows that both feldspars have near maximum disorder, as expected from their paragenesis; the high sanidine plots near the K end-member, and the albite plots between high albite and high sanidine in composition.

The analysis of the G-1 standard granite provided a more rigorous test of the method and involved analysis for four phases. The results for quartz, albite, microcline, and biotite (Fig. 8) agreed with the modes (recalculated to weight percent) of Chayes (1951) within 1 sd (Table 4) and also provided precise unit-cell parameters for all of the major phases in the rock. Data obtained using three

TABLE 4. Rietveld quantitative analysis results for the G-1 standard granite using three sample preparation methods*

	Chayes (1951)		Rietveld method		
	Mode	Norm	Smear	Filter	Packed
Quartz	27.6(1.4)	28.7(2.6)	28.2	27.3	29.1
Albite	31.2(1.4)	33.5(2.0)	31.9	32.6	32.6
Microcline	34.4(1.4)	31.7(2.8)	33.0	35.1	32.9
Biotite	3.6(0.6)	3.6**	n.d.†	1.7	2.1
Other	3.3	2.4(0.3)	n.d.	n.d.	n.d.

Note: results are in weight percent.
 * Mode and normative values of Chayes (1951) recalculated to weight percent. Rietveld results have been normalized to account for unanalyzed phases.
 ** Not determined in norm, set equal to mode value.
 † The abbreviation n.d. = not determined.

sample mounting methods gave similar quantitative results.

The prepared mixture of 50% coralline algae and 50% echinoid calcite was a test of the method's ability to separate closely overlapping contributions from similar phases. The coralline algae contained both magnesium calcite and aragonite, and the echinoid contained magnesium calcite of crystallite size and composition significantly different from the magnesium calcite in the coralline algae. Results of the Rietveld analysis (Fig. 9) gave 54(2)% echinoid calcite, 35(2)% coralline calcite, and 10.8(5)% aragonite. Use of the determinative curve of Goldsmith et al. (1961) with the cell parameters obtained for the two calcites gave a Mg content of 20 mol% for the coralline calcite and 10 mol% for the echinoid calcite. Because of peak-width variations between the two distinct calcites and severe peak overlap, compositional and quantitative phase analysis of this sample by conventional methods would be extremely difficult.

The bauxite samples were the most complex mixtures studied, with seven phases present in each sample. The first sample, from France, contained detectable goethite, hematite, gibbsite, boehmite, rutile, anatase, and kaolinite; the Hawaiian sample (CoK α data) contained hematite, goethite, magnetite, ilmenite, gibbsite, anatase, and rutile. The refinement for the first sample gave a good fit

TABLE 5. Rietveld quantitative analysis results for two bauxite samples

	French	Hawaiian
Hematite	11.9(2)*	5.5(3)
Goethite	9.5(2)	29.9(1.7)
Magnetite	n.d.**	7.7(3)
Ilmenite	n.d.	0.20(6)
Gibbsite	62.7(5)	51.4(8)
Boehmite	12.6(2)	n.d.
Rutile	0.44(5)	0.17(8)
Anatase	1.51(6)	5.2(2)
Kaolinite	1.4(2)	n.d.

Note: results are in weight percent.

* Numbers in parentheses represent the estimated standard deviation in the last quoted place.

** The abbreviation n.d. = not detected.

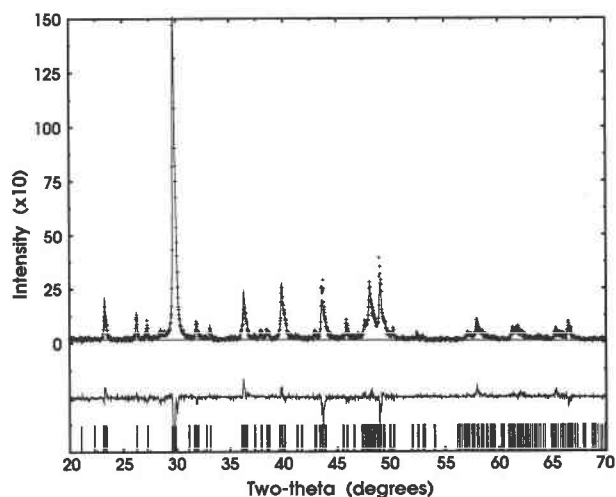


Fig. 9. Observed and calculated patterns for the 50:50 mixture of coralline algae and echinoid calcite (conventions as in Fig. 1; $R_{wp} = 21.9\%$, $R_{exp} = 14.5\%$).

($R_{wp} = 16.3$, $R_{exp} = 9.7\%$), although the results (Table 5) may be affected by microabsorption; however, the very fine crystallite size of the iron oxides in this sample will minimize microabsorption effects. Results for the Hawaiian sample ($R_{wp} = 12.7$, $R_{exp} = 11.9\%$) are in good agreement with results obtained by R. Jones using profile refinement and conventional methods (Jones and Bish, 1991) and should not be affected by microabsorption due to the use of CoK α radiation. It is noteworthy that the small amounts of rutile and ilmenite in these samples were reproducibly determined, and it appears that this method is well suited to analyzing for minor components.

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