The Rietveld method applied to quantitative phase analysis of minerals containing disordered structures

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ABSTRACT

The Rietveld method was successfully used for the quantitative phase analysis of zeolitized rocks containing montmorillonite, a phase in which the atomic positions cannot be determined exactly. The freely distributed program *FULLPROF was used in its profile-matching mode with* $Cu_{K\alpha}$ *X-ray data. This program permits carrying out quantitative* analysis without using structural data for one of the phases. This method was applied to a set of reference mixtures of kaolinite and quartz, in order to show its effectiveness compared to normal refinement. The composition of these synthetic mixtures covered the range between 10 wt% and 90 wt% of both components. The absolute errors were lower than 5 wt%. Also, a set of artificial mixtures of quartz, clinoptilolite, and montmorillonite were quantified with the profile-matching mode applied to montmorillonite. The absolute errors were lower than 6 wt%. Ten different measurements and refinements were carried out on one of these samples to obtain estimates of the true standard deviations of the concentrations. The average error values obtained are similar to the error reported by the FULLPROF program from a single refinement. The application of the method to two zeolitized tuffs of the Chubut Group, Patagonia, Argentina, with different percentages of clinoptilolite, quartz, feldspars, and clay minerals resulted in an absolute error of 3 wt% (compared to the results estimated by chemical and thermogravimetric analysis). For the zeolite phase (clinoptilolite), it was necessary to refine the occupation parameters of the exchangeable cations and the structural water molecules. The results indicate that quantitative analysis by the Rietveld method, using the FULLPROF program in the profile-matching mode for one of the phases, may be used as a routine tool for the characterization of mineral samples that contain phases with disordered structures.

Key words: Rietveld method, Quantitative analysis, Disordered structures, Clinoptilolite, Montmorillonite.

Revista Geológica de Chile, Vol. 30, No. 1, p. 103-115, 7 Figs., 6 tables, July 2003

RESUMEN

El método de Rietveld aplicado al análisis cuantitativo de fases minerales con estructuras desordenadas. El método de Rietveld fue utilizado con éxito para el análisis de fases cuantitativo de rocas ceolitizadas conteniendo montmorillonita, fase en la cual las posiciones atómicas no pueden determinarse exactamente. El programa de distribución gratuita FULLPROF fue utilizado en su modo 'profile-matching' con datos de difracción de rayos X obtenidos con radiación de $Cu_{K\alpha}$. Este programa posibilita la realización del análisis cuantitativo sin usar datos estructurales para una de las fases. Este método se aplicó a un conjunto de mezclas de referencia de caolinita y cuarzo para mostrar su efectividad comparada con el refinamiento convencional. La composición de estas mezclas sintéticas cubrió el rango entre 10 y 90% en peso de ambos componentes. Los errores absolutos fueron menores que 5% en peso. También se analizó un conjunto de mezclas artificiales de cuarzo, clinoptilolita y montmorillonita con el modo 'profile-matching' aplicado a la montmorillonita. Los errores absolutos fueron menores que 6% en peso. Para obtener estimaciones de las verdaderas desviaciones estándar de las concentraciones se realizaron diez mediciones y refinamientos diferentes sobre una de estas muestras. La aplicación del método a dos tobas ceolitizadas del Grupo Chubut, Patagonia, Argentina, con diferentes proporciones de clinoptilolita, cuarzo, feldespatos y argilominerales, presentó un error absoluto de 3% en peso (comparados con los resultados estimados a partir del análisis químico y termogravimétrico). Para la ceolita (clinoptilolita) fue necesario refinar los parámetros de ocupación de los cationes intercambiables y de las moléculas de agua. Los resultados indican que el análisis cuantitativo por el método de Rietveld con el programa FULLPROF en el modo 'profile-matching' para una de las fases, puede usarse como una herramienta rutinaria en la caracterización de muestras minerales que contienen fases con estructuras desordenadas.

Palabras claves: Método de Rietveld, Análisis cuantitativo, Estructuras desordenadas, Clinoptilolita, Montmorillonita.

INTRODUCTION

Synthetic zeolites are used in several applications. However, this is not the case for natural ones (despite their lower cost and other advantages), not only because they are multiphase mixtures but also because their homogeneity (needed for specific uses) cannot be assured. Quantitative phase analysis (QPA) of natural samples is important because of the influence of non-zeolitic components, which (even though they may not be present in great proportion) influence the physicochemical behavior of the natural compounds.

Among the traditional methods for quantitative phase analysis, X-ray diffraction techniques are widely used (Klug and Alexander, 1974; Chung, 1974a; Chung, 1974b). They are based on the fact that the intensities of diffraction peaks from a given phase are related to the phase abundance in a mixture. These methods use integrated intensities of selected reflections and need calibration curves using internal or external standards. At present, some authors have included the quantification in computational programs based on the Rietveld method for the analysis of whole powder diffraction patterns (Bish and Howard, 1988; Rodriguez-Carvajal, 1990; Young, 1993; Bergmann *et al.*, 1997).

The method developed by Rietveld (Rietveld, 1969) was created to refine crystal structures using neutron diffraction data. At present, it is one of the most powerful techniques for structural analysis, crystalline perfection studies, cell parameter measurements and quantitative analysis in X-ray powder diffraction (McCusker *et al.*, 1999). It consists of a point-to-point adjustment of the whole pattern experimental intensities (y_i^{obs}) with the calculated intensities (y_i^{cal}) based on a certain model of crystalline structure, optic effects of diffraction, instrumental factors and other characteristics of the sample. The parameters included in the chosen model are refined until the best least square fit of the thousands y_i's is obtained. The quantity minimized is the residual R_y

$$R_y = \sum_i w_i (y_i^{obs} - y_i^{cal})^2 \qquad 1$$

where

$w_i = 1/y_i^{obs}$ in the least square refinement (standard method) or $w_i = 1/y_i^{cal}$ (maximum likelihood

refinement), and the sum is overall the points of the X-ray diagram, with the calculated intensities at a given 2θ angle (y_i^{cal}) obtained by summing the contributions from background and all neighboring Bragg reflections (K) for all phases (p) as:

$$y_i^{cal} = \sum_p S_p \sum_K L_K \mid F_K \mid^2 \phi (2\theta_i - 2\theta_K) P_K A + y_{bi} \quad 2$$

where

S_p is the scale factor for phase p, L_K contains the Lorentz, polarization, and multiplicity factors, ϕ is the reflection profile function, P_K is the preferred orientation function, A is an absorption factor, F_K is the structure factor for the k-th Bragg reflection, and y_{bi} is the background intensity at the i-th 2θ angle.

The fit of the calculated pattern to the observed data can be expressed numerically by the agreement indices or R values. The weighted-profile R_{wp} value is defined as:

$$R_{wp} = 100 \sqrt{\frac{\sum_i w_i (y_i^{obs} - y_i^{cal})^2}{\sum_i w_i (y_i^{obs})^2}} \quad 3$$

For a good refinement, the final R_{wp} should be similar to the expected R_{exp} value:

$$R_{exp} = 100 \sqrt{\frac{(N - P + C)}{\sum_i w_i (y_i^{obs})^2}} \quad 4$$

where

N is the total number of used points, *P* is the number of refined parameters and *C* is the number of constrains.

Typical values of R_{wp} range from a few percents for very good neutron pattern refinements to 15-30% for laboratory X-ray data, depending on the counting time of the data collection used, the degree of preferred orientation and the number of refined parameters.

To perform QPA, the weight fraction W_i of each phase can be calculated from the scale factor S_i according to (Hill and Howard, 1987):

$$W_i = \frac{S_i (ZMV)_i / \tau_i}{\sum_j S_j (ZMV)_j / \tau_j} \quad 5$$

where

the summation is performed overall the phases, and S_i is the scale factor, Z_i is the number of molecules per unit cell, M_i is the molecular mass, V_i is the unit cell volume and t_i is the Brindley particle absorption contrast factor (Brindley, 1945).

As the Rietveld method uses a whole pattern-fitting algorithm, its application to QPA provides many advantages over traditional methods that utilize a small set of reflection lines: a) neither internal nor external standards for calibration are necessary; b) the effects of preferred orientation are reduced and the programs include appropriate parameters to be refined as part of the analysis; c) overlapped reflections are handled separately; d) mass absorption effects can be included in the refinement.

Among other authors, O'Connor and Raven (1988); Taylor and Matulis (1991); Bish and Post (1993); Weidler *et al.* (1998); Raudsepp *et al.* (1999); Gualtieri (2000) and De la Torre *et al.* (2001) used different Rietveld programs to carry out quantitative phase analysis (QPA) of mineral samples. In a conventional Rietveld refinement for multicomponent samples, the input data include space group symmetry, atomic positions, site occupancies and unit-cell parameters. Therefore, the crystal structure of each phase needs to be known in order to generate a calculated pattern that will be refined against the measured X-ray diffraction pattern. This is a disadvantage when the structural data for a given phase are imperfect or unknown. Le Bail *et al.* (1988) described a whole powder pattern-fitting algorithm, which does not need any structural model, where the angular position of the reflections was constrained to be consistent with the space group and the cell parameters. This algorithm has been implemented as an option in some Rietveld programs as FULLPROF (Rodríguez-Carvajal, 1990) of free distribution and used in this study. In FULLPROF, this Rietveld refinement mode is called 'profile-matching'. Taylor and Rui (1992) described a procedure in which the conventional Rietveld approach is modified to permit the use of observed profile data for those phases with unknown or poorly known crystal structure. Their method was tested for the case of a mineral containing pseudo-rutile.

In this work, the FULLPROF program (Version 1.9c of March 2001) was used to quantify two

zeolitized tuffs containing montmorillonite, whose atomic positions are not known with certainty. Montmorillonite is a 2:1 phyllosilicate of the smectite group stacked in a disordered fashion and with disordered extra-framework cations and water molecules in the interlayer region.

Prior to the study of the mentioned samples, artificial mixtures containing high percentages of poorly crystalline kaolinite and quartz were studied in order to compare the results obtained through two methods: the conventional method using the atomic coordinates and the profile-matching method in which the structure factors of the disordered phase are calculated from the observed intensities of a reference sample and then used in each of the analyzed samples.

To test the applicability of the profile-matching mode to samples containing montmorillonite, reference mixtures containing clinoptilolite (a tectosilicate of the zeolite group), quartz, and montmorillonite were prepared. One of these reference mixtures was mounted and irradiated 10 independent times. The respective patterns were refined to obtain an estimate of the true standard deviations of the observed concentrations.

Finally, the method was applied to two zeolitized tuffs of the Chubut Group, Cerro Barcino Formation, Patagonia, Argentina, with different percentages of clinoptilolite, quartz, feldspars and clay minerals. The obtained results were compared to the values estimated by chemical and thermogravimetric analysis.

EXPERIMENTAL CONDITIONS AND SAMPLES

The X-ray diffraction patterns were obtained in a Philips 3020 goniometer using Ni-filtered $Cu_{K\alpha}$ radiation (40 kV, 30 mA). The samples were mounted in an aluminum sample holder. Step-scan data were collected from 3 to 60° 2θ, with a step width of 0.02° and a counting time of 2 sec/step. The divergence, receiving, and scattering slits were 1, 0.2 and 1°, and no monochromator was used.

Artificial mixtures of kaolinite-quartz were prepared from 10-90 wt% up to 90-10 wt%, in 10 wt% increments. Kaolinite was supplied by Fisher Scientific Company (Georgia, U.S.A.), and was completely free of quartz. The quartz fraction used (standard from Barker, Argentina, < 325 mesh or < 45 μm) was obtained by grinding and sieving, making certain that all sediment passed through the screen. The samples were prepared and homogenized, mixing first both minerals in an agate mortar for 10 minutes with acetone until its evaporation.

Seven artificial mixtures of clinoptilolite-montmorillonite were also prepared, with different compositions between 10 and 90 wt% of each component. These mineral species were chosen due to their presence in the rocks under study. The standard clinoptilolite was obtained from a La Rioja (Argentina) chonite. This rock is composed of 5 wt% quartz and 95 wt% clinoptilolite. A size fraction smaller than 1 mm was ground and sieved so that all grains could pass through a 325 mesh sieve. The montmorillonite from Lago Pellegrini, Río Negro, Argentina (Lombardi *et al.*, 1998) was a <2 μm fraction composed of 99 wt% montmorillonite and 1 wt% quartz. The mineralogical composition of these standards were determined by X-ray diffraction. These seven artificial mixtures were also prepared and homogenized by mixing both minerals in an agate mortar with acetone until its evaporation. They were kept under controlled humidity conditions (55%). These samples are named QCM due to their quartz, clinoptilolite, and montmorillonite content and, between brackets, their respective weight percentage.

The zeolitized rocks chosen to be quantified by the Rietveld method are classified as primary tuffs. They correspond to the Cerro Barcino Formation (Chubut Group, Chubut Province, Los Altares area, Patagonia, Argentina), Upper Cretaceous in age (Manassero *et al.*, 2000). Petrographic analysis showed that the vitroclasts were altered by diagenetic processes to smectite and/or zeolites (clinoptilolite, Si/Al>4), identified by X-ray diffraction, scanning electron microscopy (SEM), and electron probe microanalysis (EPMA) (Zalba *et al.*, 1998). These samples (A10 and A40) are of great interest because of their high clay content (mostly montmorillonite), making impossible their quantification by Rietveld analysis in the traditional mode. The chemical composition of the analyzed samples was determined by the analytical technique Instrumental Neutron Activation Analysis (INAA) in ACTLABS (Canada).

RIETVELD REFINEMENT

Kaolinite is triclinic (C1) with unit-cell parameters a=5.153 Å, b=8.941 Å, c=7.403 Å, α=91.692°, β=104.860°, and γ=89.822°. The atomic positions were obtained from Bish and Von Dreele (1989), and correspond to a well-ordered structure. In natural samples, kaolinite exhibits crystalline defects (Plançon and Zacharie, 1990). These defects generate diffraction patterns whose characteristics differ from those obtained from ordered structures. For kaolinite, modulation effects and broadening of the 02*l*,11*l* reflections (in the range 20-24°2θ), and also in the 20l, 13l reflections (34-40° 2θ), are produced (Brindley and Brown, 1980).

Clinoptilolite is a zeolite. The general formula for a zeolite proposed by Gottardi (1978) is (M_x^{+}, M_y^{2+}) $(Al_{(x+2y)}Si_{n-(x+2y)}O_{2n}).mH_2O$,where M^{+} and M^{2+} are monovalent and divalent cations, respectively. A typical unit-cell formula for clinoptilolite given by Gottardi (1978) is $(Na_3K_3)(Al_6Si_{30}O_{72}).24H_2O$. Substantial amounts of Ca^{2+}, Ba^{2+} and Mg^{2+} have been found substituting the monovalent cations. According to the chemical composition of the analyzed rocks, the occupation factors used as initial values correspond to the formula $(Na_{1.84}K_{1.76}Mg_{0.2}Ca_{1.24})$ $(Si_{29.84}Al_{6.16}0_{72})$·21.36 H_2O proposed by Koyama and Takeuchi (1977) with monoclinic space group C2/m and unit-cell parameters *a*=17.662, *b*=17.911, *c*=7.407 Å, and *b*=116.4°.

For montmorillonite the hexagonal cell constants are *a*=*b*=5.165 Å and *c*=15.54 Å (PDF entry 29-1498, Montmorillonite-15A). The starting crystallographic data of the other phases were taken from Wyckoff (1963).

For kaolinite-quartz mixtures, quartz was used to refine the shift in 2θ produced by specimen displacement and the background as well. Because the cross section of the sample is smaller than the beam dimensions at low angles, correction of calculated intensities lower than 18° 2θ was carried out with the method supplied by the FULLPROF program ($y_i^{cal}(2\theta)=y_i^{cal}(2\theta)$ * sin(2θ)/sin(18°)). Then, a systematic parameter turn-on sequence was used for the scale factors for each phase, the cell parameters of kaolinite, the full-width-at-half-maximum (FWHM) parameters for each phase, the mixing parameter, h, of the pseudo-Voight profile function for each phase, and the parameter of the March function for the preferred orientation correction for kaolinite (parameters definitions can be found in FULLPROF User's Guide in http://www-llb.cea.fr/fullweb/powder.htm). For quartz, an average particle diameter of 20 mm was used for the calculation of particle absorption coefficient τ_i of Equation (1). The average particle diameter was calculated from the particle size distribution curve obtained from a particle size analyzer Sedigraph 5000/D Micromeritics.

The kaolinite structural defects are not modeled in the Rietveld refinement programs and this fact results in a poor fit in areas of diffraction patterns more affected by these defects. Initially, the refinement was carried out excluding the zone approximately between 20° and 24°2θ. Then, the diffraction patterns were refined once again but kaolinite was now treated with the profile-matching mode, where the fitting was carried out without using the atomic positions. The procedure is described in figure 1. For this purpose, a reference mixture was analyzed (95 wt% kaolinite and 5 wt% quartz), and the diffraction lines were indexed using the space group and the cell parameters (stage 1 in Fig. 1). From the measured intensities on this sample, the refinement was carried out until reaching nominal concentration values, obtaining the moduli of the structure factors in absolute units for the conventional cell (IFI).

These structure factors were used as the 'hkl' input file for the calculation of the integrated intensities of kaolinite in the mixtures under study (Stage 2 in Fig. 1). The scale factor of this phase was refined keeping the relative intensities constant. The other parameters, such as cell parameters, preferred orientation, profile shape, global temperature factor and asymmetry were also refined. Quartz was treated in the normal mode.

The same methodology was used for the clinoptilolite-montmorillonite mixtures. To obtain the structure factors corresponding to montmorillonite, a standard sample of sodic montmorillonite from Wyoming composed of 90 wt% montmorillonite and 10 wt% quartz was used. Due to the difference in the relative intensities of the observed and calculated patterns the occupation factors of water molecules and of the extraframework cations had to be refined for the clinoptilolite phase. Also, the preferred orientation parameter was refined, with the unique axis [020].

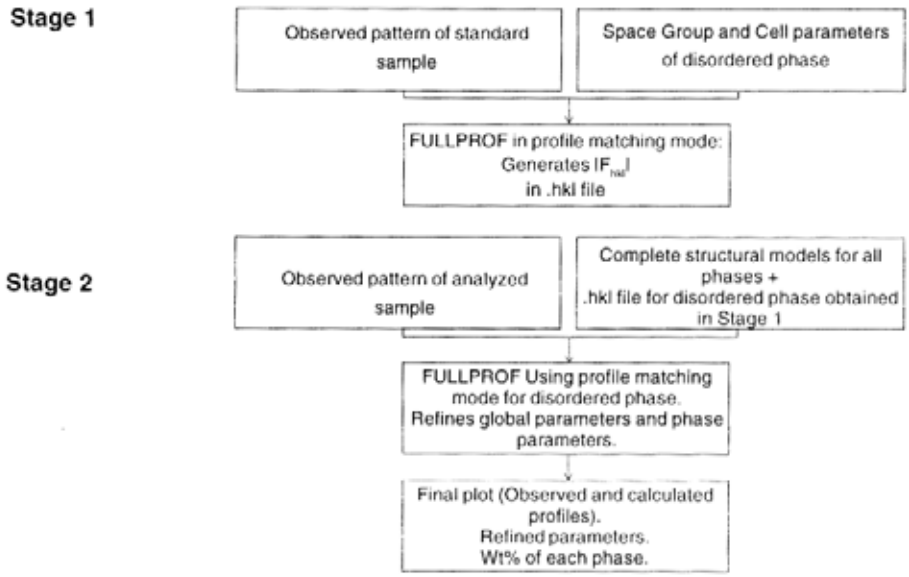

FIG. 1. Flow diagram for quantitative phase analysis with FULLPROF, including a phase in profile matching mode.

As far as samples A10 and A40 are concerned, the phases included in the refinement were quartz, clinoptilolite, oligoclase, sanidine, kaolinite, and montmorillonite. The parameter turn-on sequence for the refinement was similar to the one used for the standard mixtures. To start the refinement, the quartz present in the sample was used as an internal standard to obtain the shift in 2θ produced by specimen displacement. Then, the other phases were added. Also in this case, the occupation factors of water molecules and extraframework cations were refined, and the preferred orientation parameter was refined with [020] as the unique axis. For the feldspars, only the cell parameters and preferred orientation parameter [020] were refined. Absorption corrections were made using an average diameter particle of 20 mm. The PM mode was applied for montmorillonite in samples A10 and A40 using the technique already described to obtain the structure factors.

THERMOGRAVIMETRIC ANALYSIS

A Netzsch STA 409c simultaneous differential thermal and thermogravimetric analyzer was used. A 200 mg sample was heated at 1000°C in a Pt-Ir crucible at 10°C/min using corundum as reference material. Taking into account the overlapping between the dehydration peaks of montmorillonite, clinoptilolite and kaolinite, only estimated quantitative values could be obtained. The criterion used to assign mass losses was the following: clinoptilolite exhibits a continuous mass loss up to 500°C of about 14 wt%, whereas montmorillonite presents its mass loss in two stages, one up to 500°C and the other between 500 and 800°C; the two stages are distinct. For montmorillonite, the mass loss in the first stage varies for different samples (Bish and Duffy, 1990), but between 500 and 800°C the variation is lower. A group of 14 pure sodic montmorillonite samples showed an average mass loss of 3.6 wt% between 500 and 800°C. The total mass loss of water for pure montmorillonite averaged 19.7 wt%. Therefore, the mass loss between 500 and 800°C was used for the quantification of the montmorillonite present in the samples. Using this calculated wt% of montmorillonite, its corresponding total mass loss was obtained. The remaining mass loss was assigned to clinoptilolite. Due to the very small proportion of kaolinite, its mass loss was not taken into account.

RESULTS

KAOLINITE-QUARTZ STANDARDS

The results for the kaolinite/quartz standards (k/q), applying the Rietveld method in its normal mode (but excluding the region where the reflections were more affected by structural disorder) are presented in the 'Rietveld' column of table 1 and in figure 2. The agreement indices R_{wp} and R_{exp} for the final least square cycles of the refinement exhibit typical values (Bish and Post, 1993). Estimated standard deviations were derived from the estimated standard deviations on individual scale factors for the respective phases, excluding other error contributions.

The results obtained using the Rietveld method in the PM mode are reported in the 'Rietveld with PM' column of table 1 and in figure 3. These data show that the two methods yield similar values. In no case was the absolute error higher than 5 wt%, and in most cases the absolute error was close to 2 wt%. The correlation between the obtained and nominal concentrations of kaolinite is illustrated in figure 4. For the Rietveld data (dotted line) the equation line is $y=1.011x+0.038$ and the correlation coefficient is 0.995. For the Rietveld with PM curve (solid line) the equation line is $y=0.988x+0.022$ and the correlation coefficient is 0.998.

TABLE 1. RIETVELD QUANTITATIVE ANALYSIS RESULTS FOR STANDARD SAMPLES OF KAOLINITE/QUARTZ (K/Q) IN CONVENTIONAL MODE (RIETVELD) AND IN PROFILE-MATCHING MODE (RIETVELD WITH PM).

k/q (wt. %)	Rietveld (wt.%)	Rietveld with PM (wt.%)
10/90	8.0(3)/92.0(7)* (R_{wp}=21.8, R_{exp}=4.9)	9.4(2)/90.6(9) (R_{wp}=18.8, R_{exp}=4.5)
20/80	15.3(6)/84.7(6) (R_{wp}=19.7, R_{exp}=4.6)	19.0(5)/81.0(9) (R_{wp}=19.6, R_{exp}=4.4)
30/70	34.2(4)/65.8(6) (R_{wp}=22.5, R_{exp}=4.8)	30.6(4)/69.4(5) (R_{wp}=22.7, R_{exp}=5.0)
40/60	41.8(6)/58.2(7) (R_{wp}=24.3, R_{exp}=4.6)	42.1(7)/57.0(9) (R_{wp}=24.7, R_{exp}=4.7)
50/50	51.1(6)/48.9(9) (R_{wp}=23.2, R_{exp}=4.8)	51.7(5)/48.3(7) (R_{wp}=22.6, R_{exp}=5.4)
60/40	63.2(6)/36.8(7) (R_{wp}=23.2, R_{exp}=4.4)	62.2(8)/37.8(4) (R_{wp}=24.9, R_{exp}=4.8)
70/30	69.1(1)/30.6(5) (R_{wp}=30.2, R_{exp}=4.6)	71(1)/29.0(4) (R_{wp}=26.5, R_{exp}=4.4)
80/20	79.1(9)/20.9(6) (R_{wp}=28.9, R_{exp}=4.6)	78.1(1)/22.0(3) (R_{wp}=24.9, R_{exp}=5.6)
90/10	89(1)/11.0(3) (R_{wp}=30.6, R_{exp}=4.5)	88(1)/12.0(2) (R_{wp}=22.8, R_{exp}=5.6)

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

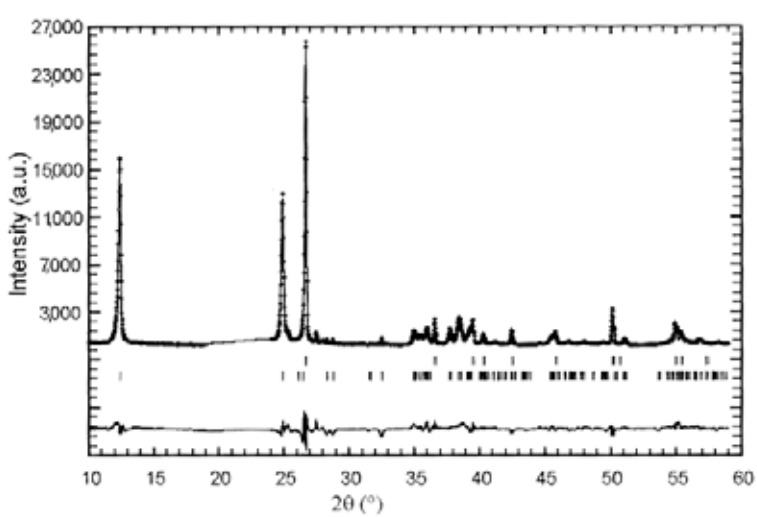

FIG. 2. Observed (dotted line) and calculated (solid line) diffraction patterns for a 70/30 kaolinite-quartz standard sample. The region between 20 and 24°2θ was excluded. (R_{wp}=30.2, R_{exp}=4.6).

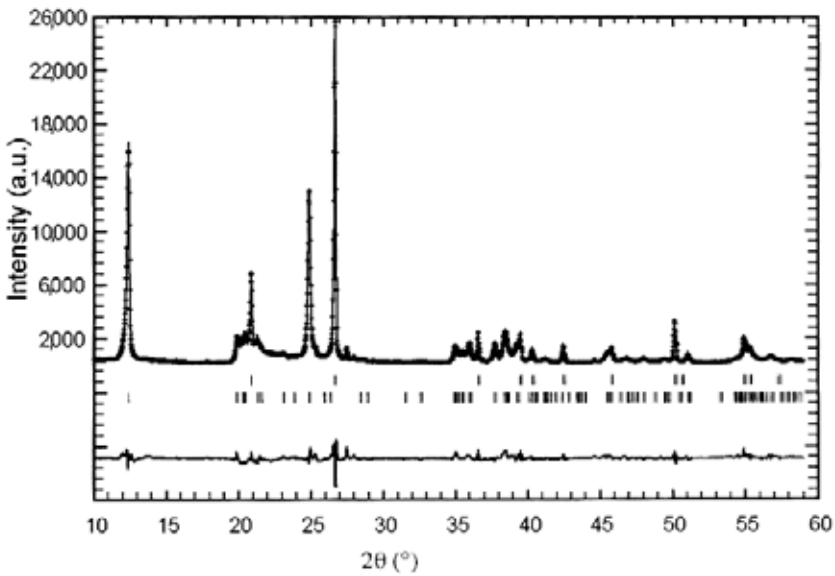

FIG. 3. Observed (dotted line) and calculated (solid line) diffraction patterns for a 70/30 kaolinite-quartz standard sample using the PM mode for kaolinite. (R_{wp}=23.5, R_{exp}=5.8).

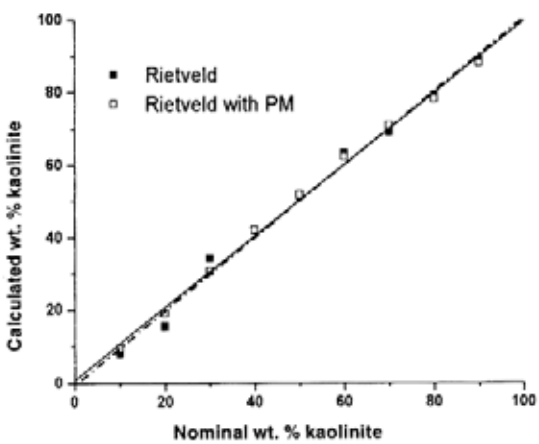

FIG. 4. Calculated *versus* nominal wt.% for kaolinite in kaolinite-quartz samples with both refinement modes (Table 1). The correlation coefficient of the Rietveld curve (dotted line) is 0.995 and of the Rietveld with PM curve (solid line) is 0.998.

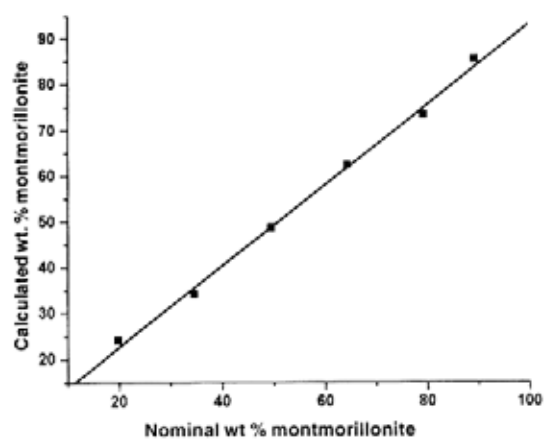

FIG. 5. Calculated *versus* nominal wt.% for montmorillonite in quartz-clinoptilolite-montmorillonite reference samples (Table 3). The correlation coefficient is 0.998.

CLINOPTILOLITE-MONTMORILLONITE-QUARTZ STANDARDS

To obtain an estimate of the true standard deviation of the observed concentrations, one reference mixture (composed of 3 wt% quartz, 47.5 wt% clinoptilolite, and 49.5 wt% montmorillonite) was measured and quantified 10 times (Table 2). The concentrations obtained for the 7 standard samples are reported in table 3. The absolute errors obtained do not exceed 6 wt%. The agreement between the observed and the nominal concentrations for montmorillonite is illustrated in figure 5. The equation line is 0.885x+0.027 and the correlation coefficient is 0.995. As shown in table 3, in the row corresponding to the QCM (3.0/47.5/49.5) sample, the average error values obtained from table 2 are similar to the error reported by the FULLPROF program from a single refinement.

TABLE 2. RIETVELD QUANTITATIVE ANALYSIS RESULTS FOR ONE STANDARD SAMPLE OF QUARTZ/CLINOPTILOLITE/MONTMORILLONITE.

Analysis No.	Quartz (wt. %)	Clinoptilolite (wt. %)	Montmorillonite (wt. %)	R values (wt. %)
1	2.8 (1)*	49.5 (5)	47.8 (6)	R_{wp}= 26.1, R_{exp}= 10.6
2	3.3 (1)	47.6 (5)	49.0 (5)	R_{wp}= 26.6, R_{exp}= 10.0
3	2.5 (1)	48.2 (5)	49.3 (7)	R_{wp}= 24.7, R_{exp}= 10.6
4	1.8 (1)	47.4 (4)	50.8 (6)	R_{wp}= 23.5, R_{exp}= 10.3
5	2.6 (1)	47.3 (4)	50.0 (6)	R_{wp}= 25.3, R_{exp}= 10.7
6	0.9 (1)	50.8 (4)	48.3 (6)	R_{wp}= 22.8, R_{exp}= 10.2
7	5.3 (8)	46.1 (5)	48.6 (7)	R_{wp}= 23.1, R_{exp}= 10.7
8	2.9 (1)	49.4 (4)	47.7 (6)	R_{wp}= 23.8, R_{exp}= 11.6
9	4.4 (1)	48.7 (5)	46.9 (6)	R_{wp}= 25.9, R_{exp}= 10.9
10	3.6 (1)	48.6 (4)	47.8 (6)	R_{wp}= 23.9, R_{exp}= 11.1
Average	3.0 (4)	48.4 (4)	48.6 (4)	

Note: Nominal values in wt %: quartz 3.0, clinoptilolite 47.5, montmorillonite 49.5.
* Values in parenthesis represent estimated standard deviations in the last quoted place.

TABLE 3. RIETVELD QUANTITATIVE ANALYSIS RESULTS FOR STANDARD SAMPLES OF QUARTZ/CLINOPTILOLITE/MONTMORILLONITE.

Sample	Quartz (wt. %)	Clinoptilolite (wt. %)	Montmorillonite (wt. %)	R values
QCM (1.4/9.5/89.1)	1.1 (1)*	13.4 (5)	85.5 (1.2)	R_{wp}= 31.4, R_{exp}= 17.4
QCM (1.8/19.0/79.2)	2.1 (1)	24.5 (4)	73.4 (1.0)	R_{wp}= 25.2, R_{exp}= 11.4
QCM (2.4/33.3/64.3)	1.6 (1)	36.1 (4)	62.4 (6)	R_{wp}= 24.9, R_{exp}= 13.2
QCM (3.0/47.5/49.5)	3.0 (4)**	48.4 (4)**	48.6 (4)**	
QCM (3.6/61.8/34.6)	3.3 (1)	62.7 (5)	34.0 (5)	R_{wp}= 23.0, R_{exp}= 10.5
QCM (4.2/76.0/19.8)	3.6 (1)	72.4 (6)	24.0 (6)	R_{wp}= 25.2, R_{exp}= 10.3
QCM (4.6/85.5/9.1)	5.5 (1)	80.7 (6)	13.8 (4)	R_{wp}= 21.2, R_{exp}= 9.3

* Values in parenthesis represent estimated standard deviations in the last quoted place.
** Average values from table 2.

ZEOLITIZED TUFFS

In zeolitized tuffs A10 and A40 the predominant phase is quartz. In sample A10, very little kaolinite was observed, and traces of mordenite (another zeolite species) were detected by scanning electron microscopy (SEM), but the corresponding lines were not observed in the X-ray diffraction pattern. Therefore, this last phase was not included in the Rietveld analysis. Bulk chemical analysis (Table 4) indicated that sample A40 contains 1.9 wt% Fe_2O_3. However, a crystalline phase containing Fe was not detected by XRD. Nevertheless, petrographic analysis of thin sections showed the presence of cavities infilled by clays (montmorillonite) and surrounded by Fe_2O_3 (interpreted as former holes left by roots). The distribution of these red spots was not homogeneous, resulting in a difficult quantification of the observed phases. Petrographic analysis also showed that all the glass-shards were completely transformed into clinoptilolite (Manassero *et al.*, 2000).

For these rock samples the montmorillonite had to be treated in the PM mode to use the Rietveld method. The other phases could be modelled by the traditional method.

Quantitative analysis results for sample A10 are presented in table 5. The DTA-TGA curves for this sample showed a mass loss of 7.6 wt% up to 500°C and 1.4 wt% between 500 and 800°C. The approximation used in this case allowed us to estimate concentrations of 27.8 wt% montmorillonite, and 20.9 wt% clinoptilolite.

From whole rock chemical analysis and expressing the molecular formula of each phase in oxides, an equation system was developed in order to calculate quartz and feldspar concentrations. The values obtained by TGA for clinoptilolite and montmorillonite were used in conjunction with the bulk analysis to calculate these concentrations.

The Rietveld quantitative analysis (R_{wp}=19.8 and R_{exp}=8.7, Table 5) agrees well with the results obtained by other analytic techniques. The refined values of the montmorillonite cell parameters were a=b=5.18 Å and c=15.74 Å. The observed and calculated X-ray diffraction patterns for this sample are shown in figure 6.

TABLE 4. CHEMICAL COMPOSITION OF ZEOLITIZED TUFFS A10 AND A40, CERRO BARCINO FORMATION.

	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	LOI
A10	72.62%	10.82%	1.00%	1.05%	1.56%	2.28%	1.35%	0.37%	8.90%
A40	74.47%	9.61%	1.90%	1.22%	0.93%	2.13%	0.80%	0.17%	9.23%

TABLE 5. QUANTITATIVE ANALYSIS RESULTS FOR ZEOLITIZED TUFF A10, CERRO BARCINO FORMATION. DIFFERENTIAL THERMAL AND THERMOGRAVIMETRIC ANALYSIS (DTA AND TGA), CHEMICAL ANALYSIS (CHA) AND RIETVELD METHOD.

Mineral	DTA and TG (wt.%)	ChA (wt.%)	Rietveld (wt.%)
Quartz		35.5	37.5 (3)*
Clinoptilolite	20.9		22.8 (3)
Oligoclase		11.8**	7.7 (2)
Sanidine			2.6 (2)
Montmorillonite	27.8		27.9 (4)
Kaolinite			1.4 (2)

* Values in parenthesis represent estimated standard deviations in the last quoted place.
** Oligoclase + Sanidine.

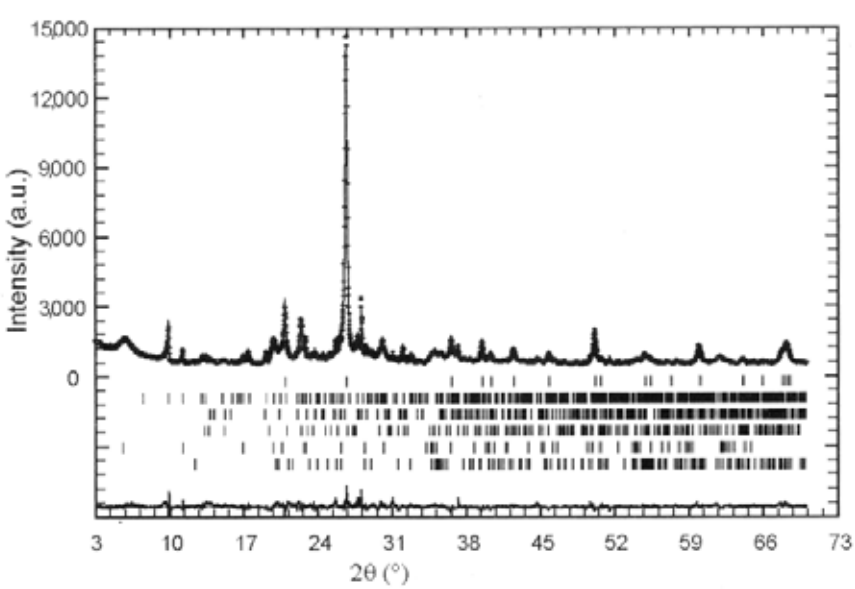

FIG. 6. Observed (dotted line) and calculated (solid line) diffraction patterns for zeolitized tuff A10, Cerro Barcino Formation (R_{wp}=19.8, R_{exp}=8.7).

The quantitative analysis for sample A40 can be observed in table 6. The DTA-TGA curves for this sample showed a mass loss of 7.0 wt% up to 500°C and of 1.2 wt% between 500 and 800°C. This fact implies a montmorillonite content of 33.3 wt% and a clinoptilolite content of 11.7 wt%. As in sample A10, the whole rock chemical analysis was used to obtain weight fractions of quartz and feldspars. Also in this case, the results obtained by Rietveld analysis (R_{wp}=16.3 and R_{exp}=8.2) are in good agreement with the results obtained by other analytical techniques. The refined values of the montmorillonite cell parameters were *a*=*b*=5.18 Å and *c*=15.45 Å. The observed and calculated X-ray diffraction patterns for this sample are shown in figure 7.

TABLE 6. QUANTITATIVE ANALYSIS RESULTS FOR ZEOLITIZED TUFF A40, CERRO BARCINO FORMATION. DIFFERENTIAL THERMAL AND THERMOGRAVIMETRIC ANALYSIS (DTA AND TGA), CHEMICAL ANALYSIS (CHA) AND RIETVELD METHOD.

Mineral	DTA and TG (wt.%)	ChA (wt.%)	Rietveld (wt.%)
Quartz		44.4	48.7 (5)*
Clinoptilolite	11.7		22.8 (3)
Oligoclase		5.8**	7.7 (2)
Sanidine			2.6 (2)
Montmorillonite	27.8		27.9 (4)
Kaolinite			1.4 (2)

* Values in parenthesis represent estimated standard deviations in the last quoted place.
** Oligoclase + Sanidine.

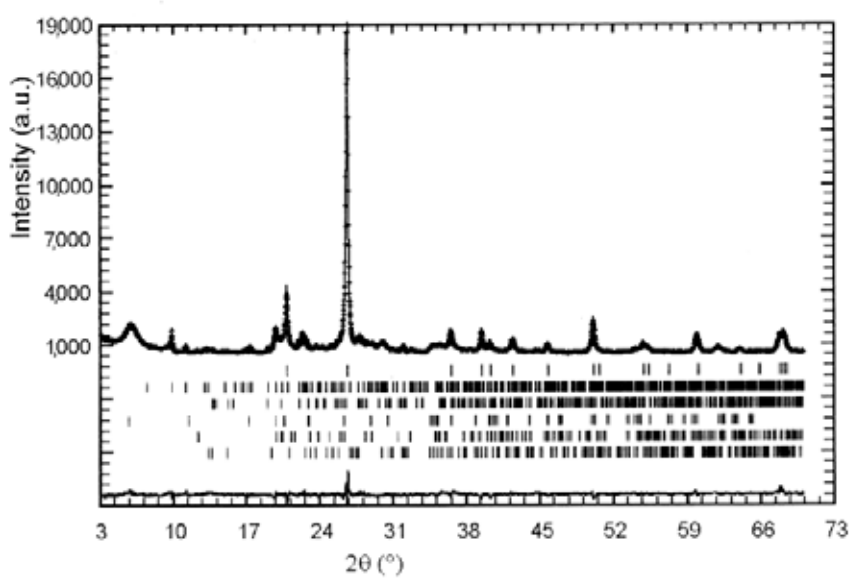

FIG. 7. Observed (dotted line) and calculated (solid line) diffraction patterns for zeolitized tuff A40, Cerro Barcino Formation (R_{wp}=16.3, R_{exp}=8.2).

CONCLUSIONS

An accurate and rapid quantification of mineral samples in rock analysis is a long-standing problem in geology. The good results obtained from standard samples and from two analyzed zeolitic tuffs, which contain clinoptilolite and montmorillonite, confirm the usefulness of the profile-matching mode for the quantification of this type of rocks. For the materials analyzed here, the quantitative analysis gave good results even when the time per step was not as long as is required for structural refinements. Therefore, the quantitative analysis by the Rietveld method can be used as a routine tool by means of faster scans than those done for refinements of structural parameters.

The given results for the kaolinite-quartz mixtures confirm that the option of applying the profile-matching mode produces similar results to those obtained with the Rietveld conventional method.

The concentrations obtained for the 7 standard mixtures of quartz, clinoptilolite, and montmorillonite show that the absolute errors do not exceed 6 wt%. The reference mixture measured and quantified 10 times demonstrates that the average error values obtained and the error values from a single refinement are similar.

ACKNOWLEDGEMENT

This work was supported by Consejo Nacional de Investigaciones Científicas y Técnicas de la República Argentina, Universidad Nacional de La Plata and Comisión de Investigaciones Científicas de la Provincia de Buenos Aires. The authors gratefully acknowledge Dr. J. Kaduk (BP Amoco Chemicals) for his constructive comments that enriched the content and style of the paper. The authors also acknowledge B. Lombardi (CETMIC) and C. Volzone (CETMIC) for providing reference montmorillonite samples and N. Vega (LACEMI-CUBA) for helpful discussions. The comments of the referees U. Kelm (Universidad de Concepción), J.J. Cochemé (Université d'Aix Marseille) and C. Brime (Universidad de Oviedo) have been particularly helpful.

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Manuscript received: July 18, 2002; accepted: May 14, 2003.