APPLICATION OF THE RIETVELD METHOD IN THE REYNOLDS CUP CONTEST

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Abstract—The Reynolds Cup (RC) is a unique round-robin competition that was established by The Clay Minerals Society in 2000 to assess the level of precision and accuracy that is attainable for the mineralogical analysis of a wide range of complex clay-rich materials. Although the Reynolds Cup round-robin allows any possible analysis methods, X-ray diffraction (XRD) is by far the most frequently used technique. It is not only used to identify components, but also for quantitative phase analysis (QPA). QPA means determination of the relative concentrations of the coexisting phases in a mixture, commonly as a weight percent (wt.%) or mass fraction. Several approaches allow a quantitative determination of mineral contents, such as the Rietveld method (Rietveld, 1967). The successful application of the Rietveld method for QPA requires that all components are correctly identified and that the component diffraction patterns are appropriately described, which is preferably based on structure. In addition, the quality of a Rietveld quantification also depends on suitable sample preparation and measurement conditions, as well as a correct description of instrument configurations. Results from all previous Reynolds Cup contests show that a successful quantification depends strongly on the skill of users. Although the refinement procedure itself is automatic and, therefore, user independent, the results are strongly influenced by the structural models and refinable parameters that are selected and on the limitations of those parameters. Selected examples for the successful application of Rietveld refinement as well as the limitations of the method will be discussed in this article. The goal of the present work was to demonstrate that the Rietveld method is in principle capable of quantifying all Reynolds Cup samples with a high degree of accuracy, but sample specific difficulties and analysts' inexperience may impede successful application. Incorrect results are often not indicated simply by low residuals or good fits. All refinement results should be validated and corrected using supplementary techniques, even if the results appear acceptable.

Key Words—Quantitative Phase Analysis, Reynolds Cup, Rietveld Refinement.

INTRODUCTION

Although all mineral quantification methods are permitted in the Reynolds Cup (RC), XRD (X-ray diffraction) is by far the most frequently employed primary technique (Raven and Self, 2017). Of the 97% of participants that used XRD, almost 60% of those used any one of a number of different Rietveld programs. Whole pattern fitting methods, such as the Rietveld method, have the advantage that they do not rely on single peak intensities that often overlap with other mineral peaks, and peak intensity can be strongly affected by preferred orientation and particle size effects. The effects of preferred orientation are more or less averaged over the whole pattern if a significant amount of the mineral is present. In principle, all the mineral components in a mixture can be quantified from an XRD pattern of the bulk material. Rietveld methods would seem to be the most convenient because standards are not required to perform an analysis and automatic refinement procedures can be applied to bulk materials. Several different Rietveld programs have so far been applied to the Reynolds Cup samples. The programs were all derived from the original principle of calculating diffraction patterns from crystal structures, but differ in the methods used to describe peak shapes and widths, background functions, preferred orientation, and so on.

All Rietveld programs have specific strengths and weaknesses in terms of the mathematical treatments, usability, and functionality. Commercial products offer user friendly graphical user interfaces specifically designed for quantitative phase analysis, but are relatively expensive to purchase. Heavily discounted academic or freeware versions, which are available *via* downloadable software sites, offer access to a much wider community of users. Earlier software codes were controlled *via* input text files and required experience and detailed crystallographic knowledge. To make matters worse, not all Rietveld software programs are capable of adequately modelling the extensive disorder that is exhibited by the clay minerals. Although the refinement procedure is automatic and, therefore, user independent, the results are strongly influenced by the wide range of structural models and refinable parameters that can be selected and on the limitations of these parameters. All refinement results, whether or not statistically valid, should be confirmed and corrected or constrained by supplementary analytical techniques if necessary.

While users of Rietveld based methods represent five of the seven Reynolds Cup winners to date, a much

higher proportion of users were also the worst performers. The quality of results are, therefore, heavily influenced by the myriad of choices that are available to users and, hence, by the level of expertise.

Almost all samples from the seven Reynolds Cup contests contained minerals or combinations of minerals that are difficult to model using the Rietveld method; however, only a limited number of these will be discussed here due to the large array of difficulties. The difficulties are: (1) correct identification of all sample mineral phases; (2) the impact of background description on quantification; and (3) the modeling of disordered phases or phases with unknown structures. A performance test was preliminarily applied to evaluate the capability of the Rietveld method.

Performance test of the Rietveld method

Direct comparison of contest results over time to check performance is difficult because not all participants only used the Rietveld method and occasionally even the top results were biased by misinterpretations. In addition, the RC assessment criteria became stricter in 2010 and, consequently, direct comparison of results before and after this date is difficult. To address this issue, 21 samples from the first seven RC contests were reexamined using only the Rietveld method to estimate the accuracy of the method by comparison with the actual mineral contents. Only measurements of the bulk material were used by assuming that all minerals were correctly identified. The collection of XRD patterns date back to the competition periods and, therefore, the measurement conditions (*i.e.* instrument, 2θ range, counting time, and step size) have changed over time. Further information about the actual composition and structure of the minerals was not used because one strength of the Rietveld method is that the variation in parameters, such as atomic occupancies or lattice parameters, can simultaneously be refined with the scale factors. The structural models were as used in routine analysis without individual adjustments for the RC samples. Scale factors and peak broadening parameters were refined for all models. Preferred orientation was corrected using a spherical harmonics model for minerals which are known to exhibit this effect. Atomic positions were not refined. Lattice parameters and occupation factors were refined to reflect mineral chemical variability. The maximum and minimum limits on refinable parameters were positioned within the natural range of minerals. Several different models were used for minerals which show a wide range in structural variability. For example, six models were defined for the plagioclase feldspar group using parameters and refinement limits for the albite, oligoclase, andesine, labradorite, bytownite, and anorthite members. The actual model was chosen by visually matching peak positions. The two-theta zero shift and sample displacement factors were corrected as instrumental parameters.

The background was described using 5th and 9th order polynomial functions. Amorphous components were quantified indirectly by the addition of a well crystalline internal standard.

No additional information was used to verify the refinement results. The measurements were performed using different laboratory diffractometers with Bragg-Brentano geometry. The samples were carefully ground using a McCrone micronizing mill (Retsch, Haan, Germany) to avoid changes in composition and to reduce the effect of microabsorption as much as possible. The top loading technique was used in most cases to prepare samples and in other cases, the back loading technique was used. The Rietveld program BGMN (Bergmann *et al.*, 1998) was used for this performance test. The statistical quality of the refinements were assessed using a discrepancy index and the weighted profile R factor R_{wp}. R_{wp} was compared to the best possible R_{wp} value, called the expected R factor R_{exp} (Young, 1993). The quantification results were evaluated using the current, more stringent rules that have been used since the 2010 contest (Table 1). The bias per sample, the number of minerals N, and the bias per mineral were separately determined for clay minerals and non-clay minerals. The bias in % is defined here as the absolute value of the difference between the actual (*i.e.* weighed) content in wt.% and the submitted (*i.e.* determined) content in wt.%. The trend in total bias (*i.e.* sum bias, Table 1) steadily increased during the first seven RC contests. This approximately correlates with the increased number of minerals per sample mixture. The bias per non-clay mineral for each RC contest was usually lower than the bias per clay mineral. The average bias per non-clay mineral was just 1.1%, but the average bias per clay mineral was three times higher at 3.3%. Several possible explanations for the high bias of clay minerals are: first, sample preparation is difficult due to the platy shape of the layer silicates, which results in a strong tendency for preferred orientation; second, many clay minerals also show structural disorder effects, which are difficult to describe and model using traditional Rietveld methods; and, third, clay mineral structures are often quite similar to each other and, therefore, the diffraction patterns are correspondingly similar. These sources of bias are partly overcome by grouping the minerals in the assessment. The non-clay minerals generally show little, if any, disorder effects and are described using conventional crystallographic models. The only exceptions are for very poorly crystalline or amorphous components, such as ferrihydrite and volcanic glass.

Qualitative phase analysis

The correct identification of all components in a mixture is absolutely essential for successful application of the Rietveld method for quantitative phase analysis. The Reynolds Cup contest has shown that this is not a

Table 1. Results of the performance tests of all the past RC samples where N = the number of clay/non-clay minerals per sample and bias = the absolute value of the difference between the actual content and determined content.

Year	RC	Sample 1						Sample 2						Sample 3						sum bias
		non-clay			clay			non-clay			clay			non-clay			clay			
		bias	N	bias/N	bias	N	bias/N	bias	N	bias/N	bias	N	bias/N	bias	N	bias/N	bias	N	bias/N	
2002	1	14.6	9	1.6	11.7	3	3.9	7.4	9	0.8	3.1	3	1.0	5.8	10	0.6	2.4	2	1.2	45
2004	2	2.6	7	0.4	11	3	3.7	2.9	6	0.5	6.6	3	2.2	6.4	8	0.8	4.2	2	2.1	33.7
2006	3	10.4	12	0.9	21	3	7.0	9.9	11	0.9	6.8	3	2.3	10.7	6	1.8	4.8	4	1.2	63.6
2008	4	15	9	1.7	2.7	2	1.4	6.7	6	1.1	10	4	2.5	9.5	7	1.4	7.6	3	2.5	51.5
2010	5	5.1	9	0.6	31.1	6	5.2	7.2	10	0.7	6.3	4	1.6	10.5	9	1.2	22.7	5	4.5	82.9
2012	6	7.7	8	1.0	28.5	4	7.1	6.7	7	1.0	26.4	6	4.4	29.5	11	2.7	10.3	3	3.4	109.1
2014	7	13.3	16	0.8	7.2	5	1.4	19	11	1.7	30.5	4	7.6	14.8	13	1.1	13.5	6	2.3	98.3

trivial task (Raven and Self, 2017). In fact, many of the top finishers rarely fulfill this basic requirement. The missed identification of minerals in the sample or the misidentification of minerals not in the sample not only biases the actual mineral contents, but also negatively affects the proportions of all components in the mixture, even if the components were correctly identified. The inclusion of minerals not in the sample were not judged as additional biases in the first three RC contests because this error is implied in the content of the correctly identified minerals. For example, even if the relative proportions of all minerals in a sample were correctly determined and 10 wt.% of a mineral not in the sample was declared, the reported QPA of all other minerals is 10% low. In 2008 and later, the content of the misidentified minerals was included in the total bias, which makes the effect of an incorrectly identified mineral even more severe.

Automated search-match software is widely used for qualitative analysis. These programs consist of an automatic peak search routine and subsequent matching using a database of known crystalline phases. The resulting list of minerals that are potentially in the sample should be carefully checked by the user. Even if all peaks were explained by a matched mineral phase, the list may misrepresent the actual composition. The user has the ability to restrict the search using supporting data, such as the chemical composition. In any case, the results should be confirmed by additional analysis or assessed by information, such as the typical paragenesis of the materials.

Low concentration mineral phases are generally difficult to identify. Peaks with a low intensity may overlap strong peaks from other phases or the counting statistics might be too poor for a reliable identification. Disordered clay minerals, such as the smectites, have an additional problem in that the broad peaks at low concentrations can merge with the background. The correct identification of clay minerals is often difficult for the bulk material and an enrichment of the clay minerals by separating the fine fraction is usually required.

The effect of omitting a mineral phase is demonstrated here using the Rietveld refinement of sample 1 from the seventh RC in 2014 (Figure 1). The crystal structures of the main minerals were included in the Rietveld refinement. Five minor minerals were omitted: tourmaline (0.7 wt.%), apatite (1.1 wt.%), smectite (2.4 wt.%), illite-smectite (2.4 wt.%), and biotite (1.2 wt.%). The peaks from other minerals and the peaks of the five minor mineral phases were strongly superimposed or the disordered clay mineral peaks were broad and diffuse. Although phases that summed to 7.8 wt.% were omitted from the analysis, the fit was statistically a good one (*i.e.* $R_{wp} = 5.94\%$, $R_{exp} = 3.64\%$) and was visually acceptable (Figure 1, Table 2). This quantification led to a total bias of 25.0%, while a
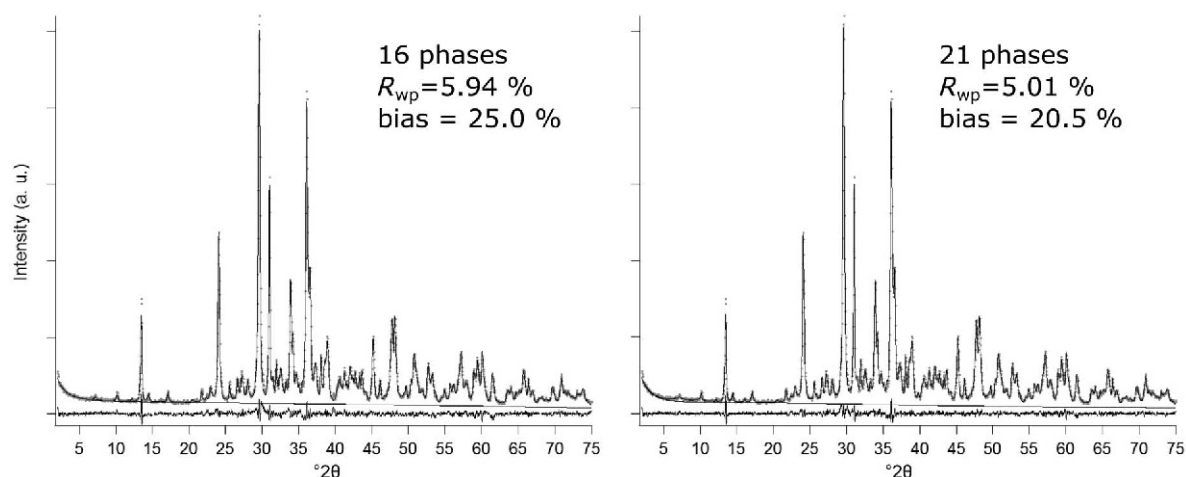
Figure 1. Rietveld refinement of sample 1 from the seventh RC in 2014 (Co Kα radiation). Refinement which ignores five of the minor phases (left) and refinement which considers all of the phases. Measurement conditions: PANalytical X'Pert PRO MPD, Co radiation, 2−75º2θ measurement range, step size 0.03º2θ, 24 s per step, automatic divergence slit (20 mm irradiated length), secondary beam graphite monochromator, and point detector.

refinement that considered all the minerals led to a better bias of 20.5% and a lower R_{wp} factor of 5.01%. The impact of two missing non-clay minerals was not as severe as the impact of the clay minerals. The main source of the discrepancy was the overestimation of muscovite and the omission of smectite, illite-smectite, and biotite. The reason is that the patterns of (disordered) layer silicates tend to correlate strongly with

Table 2. Quantitative refinement results of sample 1 from the seventh RC in 2014 with a comparison between a refinement that ignored five minor phases (left) and a refinement that considered all phases (right) with all contents declared as wt.%.

Mineral	Actual	5 minerals ignored		Complete	
		Refinement result	bias	Refinement result	bias
Quartz	5.1	6.5	1.4	6.1	1.0
K-Feldspar	2.0	2.7	0.7	2.2	0.2
Plagioclase	3.1	3.8	0.7	3.5	0.4
Pyrite	1.9	1.5	0.4	1.5	0.4
Hematite	1.0	1.8	0.8	1.3	0.3
Gypsum	21.8	20.5	1.3	19.4	2.4
Anhydrite	22.7	21.2	1.5	19.2	3.5
Bassanite	1.1	1.3	0.2	2.4	1.3
Calcite	2.4	1.9	0.5	1.8	0.6
Dolomite	16.5	18.7	2.2	17.3	0.8
Magnesite	2.6	2.3	0.3	2.5	0.1
Rutile	1.1	1.3	0.2	1.0	0.1
Tourmaline	0.7		0.7	1.5	0.8
Apatite	1.1		1.1	0.4	0.7
Celestine	1.3	0.9	0.4	0.7	0.6
Amphibole	1.4	2.8	1.4	1.5	0.1
Total non-clay	85.8	87.2		82.3	
Bias non-clay			13.8		13.3
Smectite (dioctahedral)	2.4		2.4	3.9	1.5
Illite-smectite (dioctahedral)	2.4		2.4	6.3	3.9
Muscovite	2.4	7.3	4.9	2.1	0.3
Biotite	1.2		1.2	1.0	0.2
Chlorite (trioctahedral)	5.8	5.5	0.3	4.5	1.3
Total clay	14.2	12.8		17.8	
Bias clay			11.2		7.2
Total bias			25.0		20.5

each other and also with the background function. Under ideal circumstances, inspection of the difference pattern may assist in the identification of missing mineral phases. The difference plot of the Rietveld refinement that had five omitted mineral phases showed a peak at approx. 39.7º2θ. This peak may indicate the presence of biotite. All the other missing mineral phases, however, could hardly be identified from the difference plot, even the well crystalline phases. Low concentrations of disordered clay minerals are always difficult to identify from a powder pattern of the bulk material alone. Consequently, the oversight of these minerals can not only lead to wrong quantifications, but including clay minerals that are not present in a sample in a Rietveld refinement will also bias the results. In addition, the goodness of a refinement fit does not guarantee correct results. Samples with a clay mineral concentration increased by separating the clay fraction (*i.e.* <2 μm) must be used, and additional analysis is often necessary.

Background description and amorphous content

A diffraction pattern consists of intensity contributions from both the sample and the instrument. In the case of crystalline phases, the sample-dependent part contains well defined Bragg peaks and both the sample and instrument contribute to the background. Materials with little or no long range ordering (*i.e.* XRD amorphous) show no Bragg peaks and often don't display broad or asymmetric reflections from stacking disordered structures. These materials produce one or more broad and diffuse humps, which are difficult to detect in the presence of well crystalline phases. Under certain circumstances, the humps from one amorphous material overlap the valleys of another amorphous material and increase the apparent background. Poorly resolved peaks from crystalline phases with low symmetry, such as feldspars, may also be misinterpreted as part of the background.

Dealing with the background in Rietveld refinements depends on adequately subtracting or describing the instrumental contribution without reducing the contributions of the phases that require quantification. Several methods exist to treat the background in Rietveld techniques. Some Rietveld programs require a diffraction pattern without background. In this case, the background is subtracted prior to the refinement. Other programs allow the definition of nodes, which are interpolated using different analytical functions, such as a linear function in the simplest case. The background, with or without nodes, can be analytically described to allow background parameter refinement, but these parameters have no physical meaning. The refinement as a scalable pattern can be introduced when the background and amorphous material contributions are well known and this scalable pattern can be prepared from measurement of a suitable standard material.

The Rietveld method normally requires structural data for the calculation of XRD patterns; however, the results are usually normalized to 100% (Hill and Howard, 1987; Bish and Howard, 1988). The method can also be used to indirectly determine the amount of amorphous materials (Madsen *et al.* 2011). In order to do this, the sample is spiked with a well crystallized material, such as corundum, which has a suitable crystallite size and a low absorption contrast. This added phase, however, will systematically be overestimated if amorphous materials are present. The amorphous content of the unspiked sample, c(amorph), can be recalculated from the refined standard content, c(Rietveld), using Equation 1, where c(standard) is the known true content accurately weighed (typically 10−50%) into a weighed amount of the sample material. When the refined Rietveld standard concentration (c(Rietveld)) is less than the weighed concentration (c(standard)), a physically meaningless negative amorphous content is calculated (Equation 1).

$$c(\text{amorphous}) =$$
$$\frac{100 \text{ wt.\%}}{100 \text{ wt.\%} - c(\text{standard})} \cdot 100 \text{ wt.\%} \cdot (1 - \frac{c(\text{standard})}{c(\text{Rietveld})})$$
$$(1)$$

Sample 3 from the fifth RC (2010) contained 18.3 wt.% amorphous material, which was very difficult to detect because it consisted of a mixture of allophane and ferrihydrite (Figure 2). The humps and valleys of these two materials overlap to produce a more intense apparent background, which lacks the distinctive amorphous hump. Sample 3 also contained kaolinite with disordered stacking and turbostratically disordered saponite. The XRD reflections of these two minerals are broad, modulated, and also correlate with the refined background function. In this refinement, the minerals were described using a disorder model for saponite according to Ufer *et al.* (2004) and a list of empirical *hkl*-dependent peak parameters for kaolinite. In the refinement pattern (Figure 2), the background was described using a 7th order polynomial function. Corundum (20 wt.%) was added to the sample and the Rietveld analysis refined value was 23.4 wt.%. This was recalculated using equation 1 as an 18.3 wt.% amorphous material content, which was in close agreement with the known addition. Also, the saponite result only had a bias of 1.1%. Unfortunately, correct quantification strongly depends on the degree of the polynomial function chosen for the background description.

In order to test the effect of the polynomial function order on the polynomial fit to the background, the sample refinement was performed 11 times (Table 3). Polynomial functions with orders less than 4 were not able to reproduce the intensity increase at low angles (*i.e.* <20º2θ). This problem can generally be overcome by choosing a higher starting angle for the refinement,
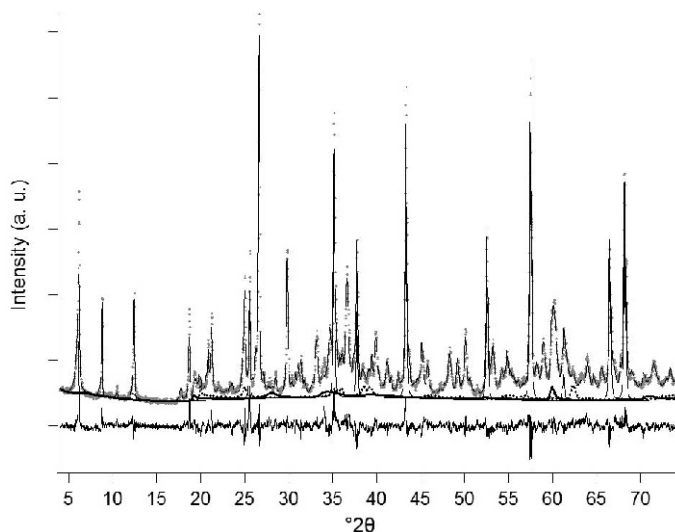
Figure 2. Rietveld refinement of sample 3 from the fifth RC in 2010 (Cu Kα radiation). Thin black line = corundum, dotted line = kaolinite, thick black line = saponite. Measurement conditions: Seifert 3000TT, Cu radiation, 4−75º2θ measurement range, step size 0.02º2θ, 20 s per step, automatic divergence slit (10 mm irradiated length), secondary beam graphite monochromator, and point detector.

but this might exclude the first basal reflections of clay minerals. Minerals with contents of 2 wt.% or less were omitted for these tests. In one case (13th order polynomial function used), the inappropriate background description could be identified by the physically senseless modulations of the background line. In other cases, the quantitative significance of the results could not be evaluated simply from the Rietveld refinements. The results that concern clay mineral and amorphous material contents strongly varied with the degrees of freedom of the background, while the variation range of

the non-clay minerals was always no more than 2.0 wt.%. The R_{wp} factors of the 10 refinements only varied between 7.4% and 7.8%. In addition to the problem of correctly describing the background, indirectly quantifying minerals mathematically using an internal standard is difficult (Westphal et al., 2009).

The performance tests of Rietveld quantification using different order polynomial functions for the background showed an average bias of 1% for the non-clay minerals. A range of ±1% should, therefore, also be considered for the added standard. Plotting the

Table 3. Quantitative refinement results of sample 3 from the fifth RC in 2010 with a comparison of refinements that used different order polynomial functions for background description. All contents declared as wt.% of the unspiked sample and the corundum content declared as the refinement result c(Rietveld) of the spiked material.

Mineral	Actual	4th	5th	6th	7th	8th	9th	10th	11th	12th	14th
Quartz	9.7	9.3	9.3	9.0	9.4	9.3	9.3	9.7	9.2	9.2	9.3
Amphibole	4.0	5.3	4.9	5.2	5.1	4.9	3.9	3.7	3.9	3.4	3.5
Epidote	4.0	3.8	3.8	3.5	3.4	3.5	3.3	3.0	3.1	3.0	3.3
Goethite	7.8	7.6	8.5	9.2	8.3	8.0	8.2	8.0	7.8	8.3	8.1
Calcite	9.1	7.6	6.6	5.6	7.2	7.3	6.4	6.4	7.1	6.4	6.7
Aragonite	3.0	2.8	2.6	2.4	2.3	2.4	2.6	2.8	2.4	2.4	2.4
Kaolinite (disordered)	6.6	9.3	9.5	12.1	9.7	9.9	10.3	9.4	10.3	9.2	8.8
Biotite	4.4	6.3	5.1	5.5	2.8	5.1	5.1	3.2	6.4	5.4	5.4
Vermiculite (trioctahedral)	11.2	16.1	17.0	16.9	15.4	15.8	17.8	16.4	15.5	17.1	16.5
Chlorite (trioctahedral)	14.2	10.6	8.2	7.5	11.9	11.4	8.2	9.2	10.7	8.4	10.4
Saponite	5.1	9.0	7.4	0.0	6.2	5.1	4.4	9.8	3.5	4.0	11.9
Amorphous group	18.3	12.3	17.1	23.3	18.3	17.3	20.4	18.5	20.1	23.2	13.8
Corundum		22.2	23.2	24.6	23.4	23.2	23.9	23.5	23.8	24.6	22.5
R_{wp} [%]		7.8	7.7	7.7	7.5	7.6	7.4	7.4	7.4	7.4	7.8
Total bias		26.8	24.0	37.0	17.4	16.8	24.5	23.5	21.0	27.2	28.5
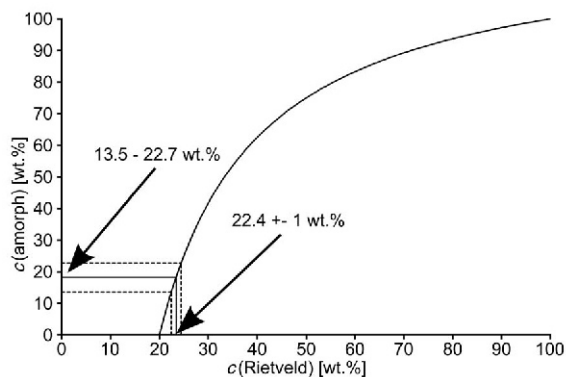
Figure 3. Relationship between *c*(amorph) and *c*(Rietveld).

relationship between *c*(amorph) and *c*(Rietveld) from equation 1 showed a steep slope in the lower part of the graph (Figure 3) when 20 wt.% corundum was added to sample 3 from the third RC in 2006 (*i.e.* 18.3 wt.% amorphous content). The Rietveld refinement can differ from the correct value for *c*(Rietveld) values of 22.4 wt.% by ±1 wt.%. Using this range of uncertainty leads to a much larger range for the amount of amorphous material of 13.5 − 22.7 wt.%. The impact of this effect is even more pronounced for materials with low amorphous material contents (Westphal, 2009).

Phases with disordered or unknown structure

All 21 Reynolds Cup samples from the seven contests contained significant amounts of disordered minerals or minerals with unknown structures, which is very common in clay mineralogy. While the extreme case of amorphous materials can be indirectly quantified as described above, the intermediate case between ordered and amorphous phases, such as stacking disorder, can no longer be described using analytical functions. In most cases, different classes of reflections can still be identified and indexed.

Materials with minor disorder can be described using the ordered equivalent structure, by introducing *hkl*-dependent peak broadening parameters, by shifting parameters of the peak position, and by using different sets of peaks to model asymmetric peak broadening (Bergmann and Kleeberg, 1998). This approach fails with stronger disorder effects, which lead to extreme asymmetric reflections and/or to a non-rational series of basal reflections. The highest degree of translational/rotational disorder is turbostratic disorder, which occurs in almost all natural smectites (Moore and Reynolds, 1997). The totally random translations and rotations of smectite layers parallel to each other prevent any coherent scattering between the layers according to the *hk*-reflections. A conventional Rietveld refinement of the published montmorillonite structure (Viani *et al.*, 2002) yielded a very poor fit (Figure 4) and had a R_{wp} value of 25.83 %.

Taylor and Matulis (1994) published a method for dealing with disordered structures by using "observed *hkl* files" that are derived from basic crystal structures and are incorporated in SIROQUANT (Sietronics Pty Ltd http://www.siroquant.com/). The procedure involves generating a series of *hkl* peaks with individual structure factors (*i.e.* intensities) using the unit cell and atom positions of a known or related crystal structure. Often the space group and the relatively small unit cells of most disordered clay minerals are not sufficient to generate enough peaks to model the broad diffraction band between 22 and 28º2θ (for Co Kα radiation). Taylor and Matulis (1994) overcame this limitation by doubling the *a* and *b* unit cell parameters and by introducing two refinable halfwidth terms to allow for both sharp and broad peaks. Structure factors are manually edited to fit an XRD pattern measured from a pure clay mineral. This process, however, disrupts the relationship between the Rietveld scale factor and the calibration factor ZMV (Z = number of formula units in the unit cell; M = molecular mass of the formula unit;
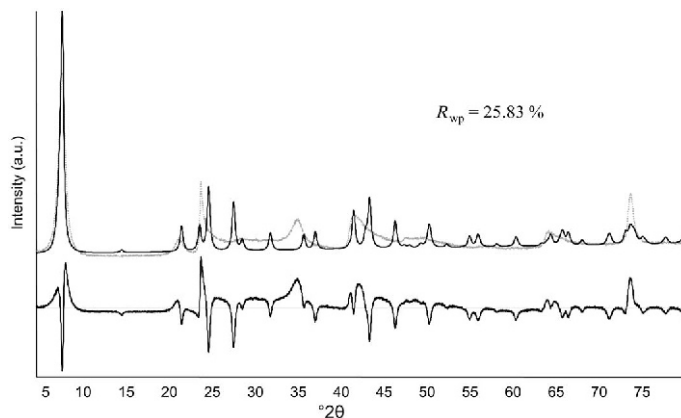

Figure 4. Conventional TOPAS refinement of the published structure for montmorillonite (Viani *et al.*, 2002) showing a poor fit with the experimental data (Co Kα radiation).
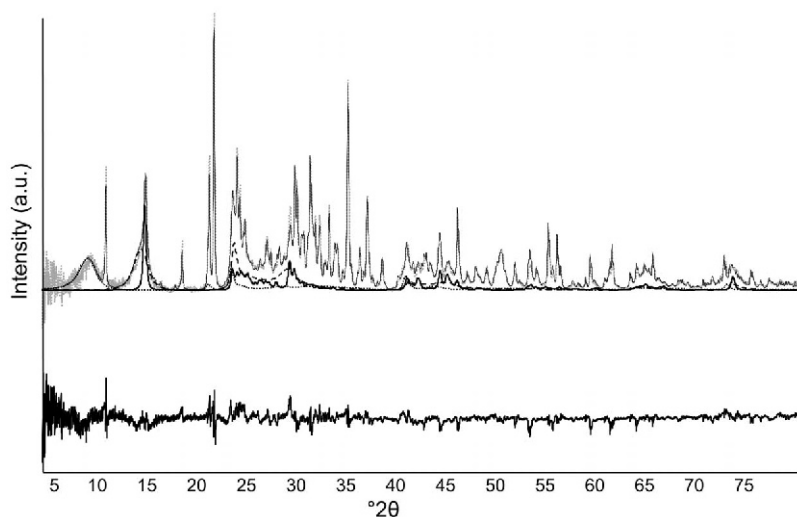
Figure 5. XRD patterns of observed (dotted gray), calculated (thin black - top), kaolinite (thick black), halloysite (dashed), and smectite (dotted black) showing a good fit to the clay and non-clay components of sample 2 from the fifth RC in 2010 (Raven and Self, 2011) using SIROQUANT (Taylor, 1991). Measurement conditions: PANalytical X'Pert PRO MPD, Co radiation, 4−80º2θ measurement range, step size 0.016º2θ, 0.5 s per step, automatic divergence slit (8.5 mm irradiated length, converted to fixed), no monochromator, and Si strip detector.

and V = volume of the unit cell) used in the quantitative analysis (Hill and Howard, 1987). Refinements of the unit cell dimensions provide the unit cell volume V, but ZM (*i.e.* the mass of the unit cell contents) must be determined by preparing several mixtures of the pure clay with an internal standard. While ZM no longer represents the true unit cell mass, it does relate to the observed structure factors (*i.e.* intensities) and, hence, to the phase concentration.

An example of the observed XRD pattern and the calculated XRD pattern that was fitted using SIROQUANT from sample 2 of the fifth RC of the winning entry in the 2010 Reynolds Cup competition is shown in Figure 5 (Raven and Self, 2011). Observed *hkl* files were created for the coexisting disordered clay minerals kaolinite, halloysite, and illite-smectite.

Quantitative analysis results (Table 4) indicate the level of accuracy that can be achieved using X-ray diffraction for the identification and quantification of complex clay-rich materials.

The observed *hkl* file technique of Taylor and Matulis (1994) has been incorporated into other Rietveld programs, such as BGMN and TOPAS (Bruker AXS, 2009). Scarlett and Madsen (2006) applied the *hkl* file technique by using TOPAS for mineral phases with either partial structures (*i.e.* only space group and unit cell known) or for no known structure at all (PONKCS − Partial Or No Known Crystal Structure). The partial structure type is essentially the same as that used in SIROQUANT, where lists of *hkl* structure factors are generated from the unit cell and space group, but atom positions are omitted (Figure 6). A much improved fit using the experimental
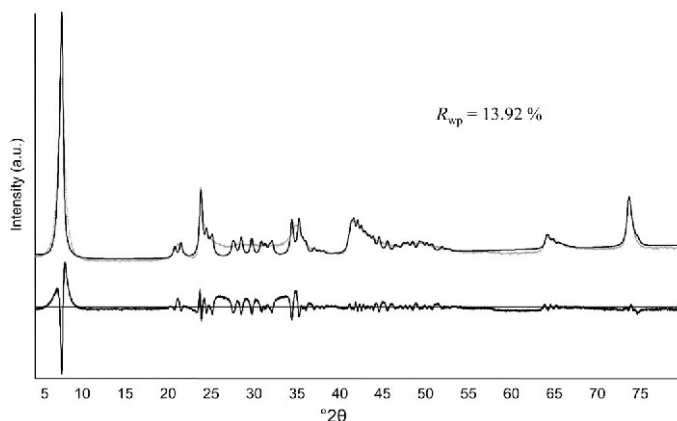

Figure 6. LeBail or *hkl* refinement of montmorillonite space group and unit cell showing a much better fit with experimental data (Co Kα radiation).

Table 4. Quantitative XRD analysis results of sample 2 from the fifth RC in 2010 using SIROQUANT (left) and BGMN (right) with all contents declared as wt.%.

Mineral	Actual	——— Siroquant ———		——— BGMN ———	
		Refinement result	bias	Refinement result	bias
Quartz	2.2	1.7	0.5	3.1	0.9
Huntite	5.0	4.4	0.6	4.8	0.2
Anatase	2.3	1.6	0.7	2.5	0.2
Alunite	10.7	9.5	1.2	11.3	0.6
Barite	5.8	4.1	1.7	6.1	0.3
Fluorite	1.9	2.0	0.1	1.9	0.0
Microcline	8.2	7.7	0.5	6.7	1.5
Albite	0.5	-	0.5	-	0.5
Gibbsite	9.6	12.0	2.4	7.0	2.6
Total non-clay	46.5	43.0		43.4	
Bias non-clay			8.2		6.8
Muscovite $2M_1$	5.1	5.6	0.5	4.4	0.7
Kaolinite	14.3	14.2	0.1	16.2	1.9
Halloysite	19.9	23.4	3.5	22.7	2.8
Illite-smectite	14.3	13.8	0.5	13.4	0.9
Total clay	53.5	57.0		56.7	
Bias clay			4.6		6.3
Total bias			12.8		13.1

data from a pure standard phase can be obtained by applying spherical harmonics to both the crystallite size and peak asymmetry for the LeBail fit (Figure 7). Since no atoms are in the unit cell, the Rietveld scale factor is independent of concentration. An empirical calibration constant is, therefore, required for quantitative phase analysis. The calibration constant is determined by preparing several mixtures of the pure clay and a 100% pure mineral (or a known concentration) crystalline internal standard (*e.g.* corundum). In the case where no structure is available, a series of individual peaks are grouped and scaled together. Because the unit cell is no longer available, the ZMV factor also must be determined using mixtures of the unknown and the internal standard.

Structurally based disorder models have an advantage over empirical fits because structural parameters are refinable and a calibration is not necessary. Turbostratic disorder can successfully be described using a supercell approach (Ufer *et al.*, 2004). Other kinds of rotational/translational stacking disorders or mixed layering can be modeled using a recursive calculation of structure factors (Treacy *et al.*, 1991) and this approach can be incorporated into the Rietveld method (Ufer *et al.*, 2008). The descriptions of disorder effects, therefore, open up the possibility of refining structural parameters. Similar issues related to traditional Rietveld refinements of structure parameters, such as the correlation effects between two or more disordered minerals in a sample,
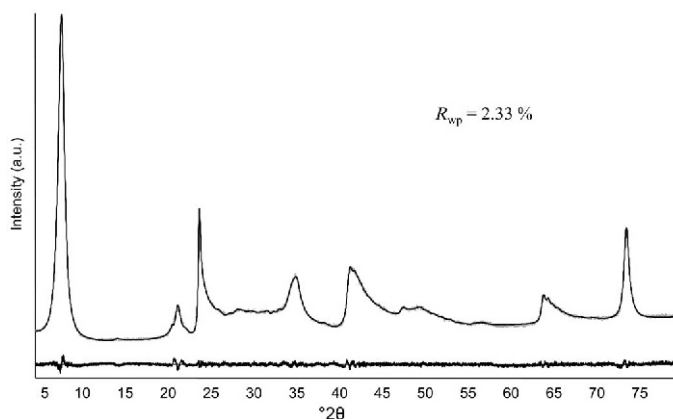

Figure 7. LeBail or *hkl* refinement of crystallite size and asymmetry using spherical harmonics showing a much improved fit with the experimental data (Co Kα radiation).

may occur with highly correlated models. Sample 3 from the third RC (2006) contains a turbostratically disordered saponite and opal-CT (Figure 8). The saponite was described by a disorder model according to Ufer *et al*. (2004), while the opal-CT was described as a stacked mixture of tridymite and cristobalite layers (Guthrie *et al*., 1995) using the recursive structure factor calculation approach.

The sample contains 35.7 wt.% opal-CT and 28.9 wt.% saponite. The Rietveld refinement led to an opal-CT content of 25.5 wt.% and 38.9 wt.% saponite. This strongly underestimated the opal-CT content, overestimated the saponite content, and resulted in a bias of 20.2% for just these two minerals. The sum of opal-CT and saponite was nearly perfectly determined as the actual sum (bias 0.2%). The total bias, however, was 28.7% due to correlations between the parameters of the two disordered minerals. The bias of all other minerals was below 2%. Again, the quality of the refined concentrations could not be evaluated by the R_{wp} factor or by an inspection of the difference patterns. The effect of strong correlations between disorder parameters, however, should be expected. A different approach, therefore, was used for the performance test of this sample (Table 1). A measured opal-CT pattern was used as a scalable background and the opal-CT content was indirectly quantified using the internal standard method and this led to a bias of only 15.5%.

In principle, stabilization of structurally based models and avoiding parameter correlations are possible by refining suitable standard minerals and by fixing or closely constraining disorder parameters. Lattice parameters or peak broadening parameters may still be refinable. In extreme cases, only scaling parameters or parameters that describe preferred orientation may be refinable. This corresponds to the use of constant structure factors, like the observed *hkl* file technique. The difference is that in the case of fixed disorder parameters, a structural model is necessary.

Sample 2 from the fifth RC was refined using the program BGMN and strongly constrained disorder models (Figure 9). Kaolinite was described using an *hkl* file generated from the standard mineral KGa-2 from the Source Clays Repository of The Clay Minerals Society (CMS). The illite-smectite was modeled by a recursive calculation of structure factors according to Ufer *et al*. (2012). Structural parameters were only refined within closely constrained limits. The halloysite was described as turbostratically disordered. This case was an oversimplification, but the model was fixed and tested by the refinement of standard mixtures. A comparison of the refinement results using SIROQUANT and BGMN showed that both programs lead to satisfying quantitative results (Table 4). While SIROQUANT was more precise for the quantification of clay minerals, BGMN allowed the refinement of structural parameters.

SUMMARY AND CONCLUSIONS

The Rietveld method has been shown to be capable of quantifying complicated mixtures like the Reynolds Cup
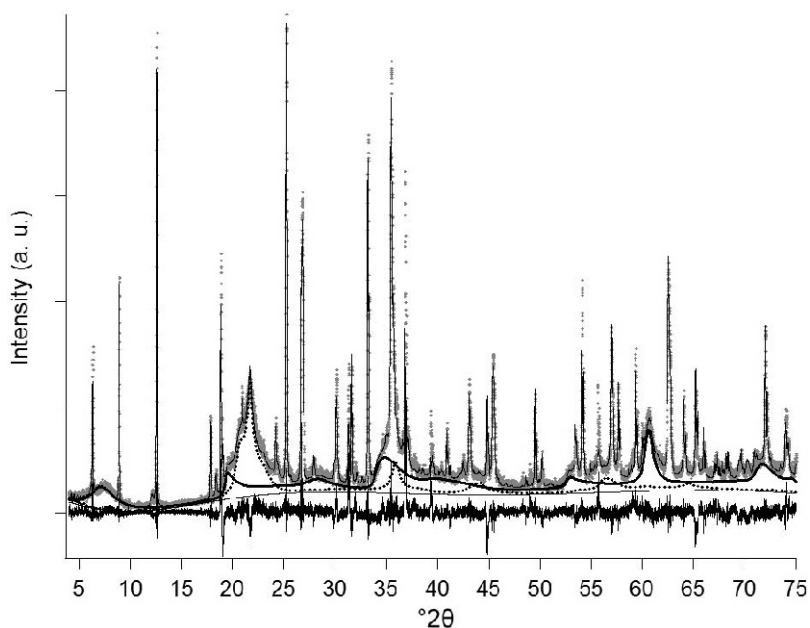

Figure 8. Rietveld refinement of sample 3 from the third RC in 2006 (Cu Kα radiation). Thick black line = saponite and dotted line = opal-CT. Measurement conditions: Bruker D8 Advance, Cu radiation, 4–75º2θ measurement range, step size 0.005º2θ, 2.5 s per step, automatic divergence slit (12 mm irradiated length), secondary beam graphite monochromator, and point detector.
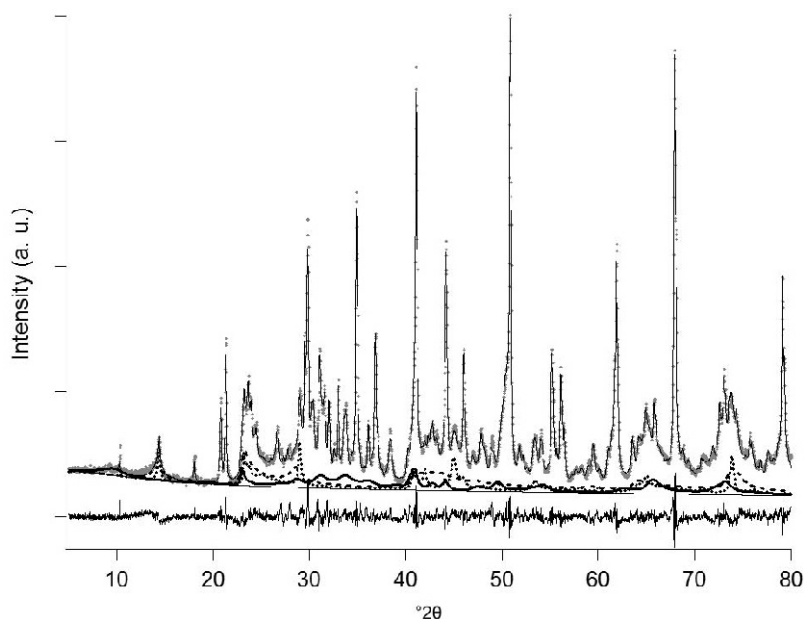
Figure 9. Rietveld refinement of sample 2 from the fifth RC in 2010. Thick black line = illite-smectite, dotted line = kaolinite, and dashed line = halloysite. The program BGMN was used here in contrast to Figure 5. Measurement conditions: Seifert-FPM URD6, Co radiation, 5−80°2θ measurement range, step size 0.02°2θ, 20 s per step, automatic divergence slit (15 mm irradiated length), secondary beam graphite monochromator, and point detector.

samples with a high degree of accuracy and precision. The refinement of XRD data from the bulk materials of the previous 21 RC samples yielded acceptable quantitative analysis results, but sample specific aspects remain an issue for many participants.

Complete and accurate identification of all mineral components (including amorphous materials) is a mandatory requirement. Accurate qualitative analysis, however, is difficult to achieve using XRD data from the bulk materials alone. Automatic search-match software needs restraints provided by additional information and the long list of possible matches should be evaluated and confirmed before progressing to quantification. This additional data can be derived, for example, from additional XRD data collected from purified subsamples obtained by size fractionation and further sample pretreatments like heat treatments. Information provided by chemical analysis can also be used to restrict misidentified phases and provide a cross-validation check during quantification.

All correctly identified phases must be accurately described for the Rietveld method by a suitable model, preferably by a conventional or disordered structural model. Non-clay minerals are less problematic and can be quantified with a typical bias of better than 1%, with the exception of amorphous phases. Amorphous phases can, however, be indirectly quantified by adding an internal standard, but this approach is highly sensitive to the correct description of the background, the amount of standard added, and the presence of highly disordered phases. Phases with unknown or highly disordered

structures can be described using *hkl* dependent lists of structure factors. This approach needs calibration using suitable reference materials. Structure based models of two or more disordered mineral phases in a sample tend to correlate if the structures are too similar and/or too many structural parameters are refined. A fixed or highly constrained model is usually required for these disordered phases.

Rietveld refinements of the XRD data for the Reynolds Cup samples have shown that statistical parameters like the R_{wp} factor or a visually good fit of measured and calculated patterns do not guarantee a satisfactory quantitative result. Excellent fits are easily obtained, but can be substantially biased by incorrect phase identification or by strong parameter correlations between several disordered minerals or with the background function. All refinement results should, therefore, be validated or constrained using supplementary techniques (*e.g.* chemistry measurements), even if the results appear satisfactory.

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