

PREFERRED ORIENTATION OF MINERAL GRAINS IN SAMPLE MOUNTS FOR QUANTITATIVE XRD MEASUREMENTS: HOW RANDOM ARE POWDER SAMPLES?

REINHARD KLEEGERG^{1,*}, THOMAS MONECKE², AND STEPHEN HILLIER³

¹ TU Bergakademie Freiberg, Institute of Mineralogy, Brennhausgasse 14, D-09596 Freiberg, Germany

² Department of Earth Sciences, University of Ottawa, Marion Hall, 140 Louis Pasteur, Ottawa, Ontario K1N 6N5, Canada

³ Macaulay Institute, Craigiebuckler, Aberdeen AB15 8QH, UK

Abstract—The degree of preferred orientation of mineral grains in powder X-ray diffraction (XRD) samples prepared by standard techniques has been evaluated by means of a correction model implemented in the Rietveld program, BGMN. It is demonstrated that neither front- nor side-loading of mineral powders obtained by wet grinding in a McCrone micronizing mill yield powder mounts with randomly oriented particles. Despite fine grinding, the primary sizes and shapes of mineral grains contained in multi-phase samples influence the degree of preferred orientation in XRD powder mounts. Two minerals, both of platy habit, were found to show different degrees of preferred orientation in front- and side-loaded samples. In contrast to these methods of sample preparation, the spray-drying technique yielded perfect randomness of the particles. The experiments on artificial mineral mixtures demonstrate that the model applied can effectively correct for preferred orientation allowing reliable Rietveld quantitative phase analysis of moderately textured samples prepared by standard techniques.

Key Words—Correction of Preferred Orientation, Quantitative Phase Analysis, Random Powder, Rietveld Method, Sample Preparation, X-ray Diffraction.

INTRODUCTION

The preparation of powder samples is, without doubt, one of the most critical steps in quantitative phase analysis by powder XRD. If inadequate sample preparation procedures are used, the relative intensities in XRD powder patterns deviate from their ideal values and are no longer only a function of structure, crystal chemistry, and concentration of the phases and instrumental parameters, but also depend on particle statistics, particle size, and preferred orientation (PO). The theoretical basis and recommendations for optimum powder preparation were summarized by Klug and Alexander (1954), Bish and Reynolds (1989), and Moore and Reynolds (1997). Those authors showed that the success of a preparation technique is strongly dependent on the properties of the multi-phase samples and that no universal procedure is applicable to a wide spectrum of sample materials.

Systematic errors may be introduced during the two basic steps of sample preparation, namely the fine grinding of the samples and the preparation of the random powder mounts. In the case of typical clay-bearing sediments and sedimentary rocks with small concentrations of highly absorbing materials (*e.g.* pyrite, hematite, or other Fe- and Mn oxides, when CuK α is

used) and without extremely sensitive water-rich phases (*e.g.* ettringite, epsomite, or similar minerals), the milling procedure is unlikely to be the most critical step. Wet milling in water, hexane, or ethanol with a McCrone micronizing mill is a widely applied technique, successfully used by many laboratories (Moore and Reynolds, 1997; Środoń, 2006). The method has been proven to produce a narrow, nominally <10 μm , particle-size distribution (O'Connor and Chang, 1986; Hillier, 2003; Dermatas *et al.*, 2007) and only introduces a minimum of structural damage. Traditional methods like dry hand-grinding in an agate mortar combined with stepwise sieving are also sometimes applied to special materials and can be successful when care is taken (Monecke *et al.*, 2001; Dermatas *et al.*, 2007).

The filling of the XRD mounts with the finely ground powders probably represents the greatest challenge during sample preparation for quantitative XRD analysis, and numerous methods have been proposed in the quest for a more or less random orientation of the particles. These techniques fall into three broad groups: (1) methods that fill untreated sample powders into sample mounts using special loading techniques; (2) procedures that involve the formation of irregular or spherical sample aggregates prior to mounting; and (3) techniques that are based on the admixing of irregularly shaped additives into the sample powders.

The methods of sample preparation belonging to the first group are particularly attractive because they are easy to apply and have the advantage that the original sample composition is preserved uncontaminated.

* E-mail address of corresponding author:

kleegerg@mineral.tu-freiberg.de

DOI: 10.1346/CCMN.2008.0560402

According to the direction of filling of the XRD mounts, front-, side-, and back-loading techniques are distinguished (Bish and Reynolds, 1989). These methods are often combined with simple tricks to produce a rough sample surface, for example by filling the holder against a roughened plate of glass (*e.g.* Moore and Reynolds, 1997), by roughening the sample surface with emery paper glued on a glass slide (*e.g.* Monecke *et al.*, 2001), by flattening the sample surface with the sharp edge of a razor blade (*e.g.* Zhang *et al.*, 2003), or by sprinkling or loosely sieving of powder onto the sample surface. Methods that are based on the formation of irregular or spherical sample aggregates involve either spraying of a sample suspension together with an organic binder like cellulose acetate into acetone or polystyrene (Flörke and Saalfeld, 1955), spraying of a sample suspension without additive (Hughes and Bohor, 1970; Hillier, 1999), freeze-drying of a slurry to form fluffy aggregates (Moore and Reynolds, 1997), or spray-freeze-drying of the sample to form spheres (Środoń *et al.*, 2001). Methods belonging to the last group of sample-preparation techniques mentioned above are less commonly used because the sample is mixed with a large volume of additives like fumed silica (Blount and Vassiliou, 1979), thermoplastic material (Brindley and Kurtossy, 1961), or cork powder (*v.* Engelhardt, 1955), all of which are undesirable from the point of view of contamination of the sample.

The benefits and drawbacks of the various techniques are subjects of endless debate. At present, methods of the second group of techniques involving the production of irregular or spherical sample aggregates by spraying or spray drying are widely accepted to produce nearly perfect randomly oriented samples. However, application of these techniques requires special equipment, time, and considerable experience. Consequently, most laboratories worldwide employ one of the simpler and less time-consuming techniques that are based on the filling of front- or side-loading mounts using untreated sample powders, although the randomness of the powder mounts and, just as importantly, the reproducibility of the sample preparation may be called into question.

Significant advances in the field may only be achieved if the degree of PO in supposedly random powder mounts is evaluated quantitatively. Although texture measurements of purposely oriented clay samples have been published and discussed in the context of quantitative phase analysis (*e.g.* Taylor and Norrish, 1966; Reynolds, 1986, 1989; Zevin and Viaene, 1990), the degree of PO in supposedly random powder mounts is only rarely measured. The lack of experiments may be explained by the extreme sample tilting required by traditional texture diffractometers, since this cannot be performed with loosely packed powders as used in phase analysis. Instead of quantitative texture measurements, so-called orientation indices are used to evaluate the degree of PO of layer silicates in powder samples (*e.g.*

Zhang *et al.*, 2003). Such indices simply represent ratios between the intensities of the basal reflections $00l$ and reflections from in-plane lattice planes such as $h00$, $0k0$, or $hk0$. Low intensity ratios indicate that the basal reflections are not pronounced, which is usually taken as a sign that the clay particles are randomly oriented.

The application of intensity ratios has two principal drawbacks. Firstly, the values obtained do not represent a direct and comparable measure of the degree of PO because the intensity ratio is also a function of structural parameters or other contributing factors such as the wavelength of the radiation and the instrumental geometry. Thus, the degree of PO can only be evaluated qualitatively, hampering rigorous comparison of different instruments and sample preparations. Secondly, the determination of orientation indices requires correctly measured intensities of individual $hk0$ reflections, which is complicated by severe peak overlap if more than one clay mineral is present in a multi-phase mixture. Consequently, the degree of PO of different minerals present in a single mixture cannot be readily evaluated by this technique.

In the present contribution, quantitative description of the PO of mineral grains in XRD powder mounts was performed using a Rietveld PO correction model. The proposed method has been used to evaluate how randomly oriented mineral grains in standard powder mounts prepared by different methods really are. For this purpose, mineral mixtures containing minerals of platy and non-platy habits, respectively, have been prepared and investigated using the front-loading, side-loading, and spray-drying techniques. Also tested are the extent to which the primary particle size of constituent phases influences the PO of particles in the powder mount following grinding in a McCrone micronizing mill and whether different platy-shaped clay minerals present in a single sample show the same degree of PO, as is commonly assumed in quantitative phase analysis (Reynolds, 1989).

EXPERIMENTAL

Analytical strategy

Based on details described in the literature and personal communications with clay scientists, the sample-preparation techniques used in the present study were designed to conform to the standard procedures used in a wide range of laboratories worldwide. However, some details obviously vary from laboratory to laboratory such as the milling time in the McCrone micronizing mill (4–12 min), the milling liquid (hexane, isopropanol, methanol, ethanol, or water), the amount of sample (2–4 g), the procedure for recovering the solid from the slurry (settling/decanting, evaporating, or filtering), the liquid/solid ratio, and the method used to destroy the aggregates of the dried powder (hand-grinding in a mortar, shaker-mill

with steel- or plastic balls, vibratory mixer mill, or manual sieving). In addition, the particulars of the actual filling procedure of the mounts vary. In the case of the commonly applied side-loading technique, for instance, critical variations include the shape and depth of the holder, the cover of the sample front (glass, frosted glass, roughened metal, or emery paper on glass), the filling technique (tapping on the table-top, use of a shaker machine or tamper), and the amount of powder contained in the holder and its bulk density. The particulars of the techniques described below are based on the personal preferences and experiences of the authors, but do not necessarily represent the best possible choice in every aspect.

Muscovite-dickite-quartz mixture

To evaluate the degree of PO in powder mounts prepared by different techniques of sample preparation, a simple three-component mixture containing muscovite, dickite, and quartz was used. Muscovite (Våne, Norway) was selected as one component because micas are common in most sediments and sedimentary rocks. Dickite (Altenberg, Germany) was chosen over kaolinite as a second component because dickite lacks the pronounced stacking disorder that makes XRD patterns of kaolinite-bearing samples difficult to refine by the Rietveld method. Investigations by scanning electron microscopy (SEM) showed, however, that the crystal shapes of the hydrothermally formed dickite flakes used as a starting material are comparable to those of well ordered kaolinite (Figure 1). Quartz (Minas Gerais, Brazil) was used as the third component of the mineral mixture.

Because sediments and sedimentary rocks commonly contain micaceous species of varying origin and particle sizes and shapes, three muscovite-dickite-quartz mixtures were prepared that differed only in the initial particle size of the muscovite component. For this purpose, the cm-sized pegmatitic muscovite crystal

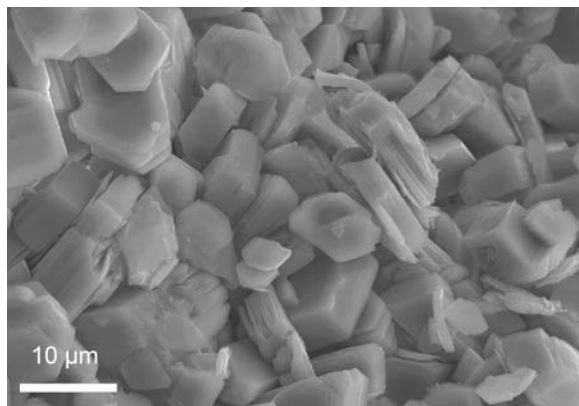


Figure 1. Secondary electron image of the dickite starting material from Altenberg, Germany.

used as a starting material was ground carefully and the resultant powder was then split into $<2\ \mu\text{m}$, $2\text{--}6.3\ \mu\text{m}$, and $6.3\text{--}20\ \mu\text{m}$ size fractions *via* sieving and gravity sedimentation. In contrast to the muscovite component, the dickite and quartz powders were not separated into different size fractions. Powders of both minerals reminiscent of such in the clay and/or silt fractions of sediments and sedimentary rocks were obtained by crushing the starting materials to a grain size of $<0.4\ \text{mm}$ followed by grinding in a McCrone micronizing mill for 5 min. Subsequently, each of the three different size fractions of the muscovite was mixed with the dickite and quartz powders at a ratio of 30:30:40, respectively.

Following the preparation of the three muscovite-dickite-quartz samples (each being 4 g of material), the mixtures were ground under 10 mL of ethanol in a McCrone micronizing mill for an additional 5 min. After drying of the slurry (evaporation of the ethanol at room temperature), the samples were homogenized in a vibratory mixer mill containing small steel balls for 4 min to destroy mineral aggregates that formed during the drying process.

Fluorite-albite-quartz mixture

A fourth mineral mixture was prepared to evaluate the extent to which non-clay minerals of primarily isometric habit, but with one or more pronounced cleavages, show PO in powder mounts. This mixture consisted of fluorite (Schönbrunn, Germany), albite (Borstendorf, Germany), and quartz (Minas Gerais, Brazil). The three starting materials were initially crushed to a grain size of $<0.4\ \text{mm}$ and then mixed at a ratio of 30:30:40. The artificial mixture obtained (4 g of material) was ground under 10 mL of ethanol in a McCrone micronizing mill for 8 min. Following drying of the slurry, the sample was homogenized in a vibratory mixer mill containing small steel balls for 4 min.

Sample mounting

In a first step, XRD mounts were prepared by filling the finely ground mineral mixtures into conventional front-loading, circular sample holders of 27 mm diameter and a filling depth of 2 mm. After loose filling of the holders, the sample surfaces were roughly flattened using the sharp edge of a glass slide. To obtain a perfectly planar sample surface, a glass slide with emery paper glued on the flat side was then cautiously pressed on the sample surface. During both steps, care was taken to apply a minimum of pressure and to avoid lateral shearing motion.

Following the XRD measurements on the front-loaded samples, the powders were removed from the holders and passed through a sieve (0.4 mm mesh) to destroy coarse aggregates that may have formed during the previous sample preparation (Środoń, 2006). The recovered powders were then filled into side-loading

sample mounts. For this purpose, circular aluminum holders (diameter of 27 mm and a filling depth of 2 mm) with 5 mm long side openings were used. During filling, the front of the side-loading holders was covered by emery paper glued on the flat side of a glass slide, which prevents particles from orienting against the plane of the glass. Adjustment of the bulk density of the powder filled into the holder was done simply by slight tapping of the holder on the tabletop. After filling the mount, the cover slide with the emery paper was removed carefully, taking as much care as possible to avoid lateral movement. Due to the theta-theta geometry of the diffractometer and the slow sample spin velocity (one rotation per second), it was not necessary to close the side openings of the holders. No powder fell out of the holders during the measurements.

To test whether spray drying does indeed yield samples lacking PO, the muscovite-dickite-quartz mixtures were recovered after measurement in the side-loaded holders and suspended in a 0.5% (w/v) aqueous solution of polyvinyl alcohol. The suspensions were prepared in small glass jars at solid to liquid ratios of ~2.0 to 2.5 and homogenized by shaking the jars by hand for 2 min, followed by 2 min of treatment in an ultrasonic bath. The samples were subsequently spray dried following the procedure described by Hillier (1999). The product recoveries ranged from 62 to 68 wt.%. The spray-dried samples, which consist of thousands of spherical powder aggregates having diameters between 50 to 60 μm , were then loaded into circular 27 mm diameter sample holders having a filling depth of 1.5 mm. Excess material was removed laterally using the sharp edge of a razor blade. The resultant samples had relatively rough surfaces and were mechanically unstable. Therefore, these samples were measured in horizontal position.

X-RAY DIFFRACTION ANALYSIS

Step-scan XRD data of the variably prepared mineral mixtures were collected on a Seifert XRD 3000 theta-theta diffractometer (angular range of 7 to 70°2 θ , step width of 0.02°2 θ /step, and an accumulation time of 8 s/step) that was equipped with a diffracted-beam graphite monochromator and an automatic divergence slit allowing the irradiation of a constant area on the rotated sample. A Cu tube was used and operated at 40 kV and 30 mA. Rietveld refinement of the XRD patterns was performed using the program BGMN (Bergmann *et al.*, 1998). The crystal-structure data used to derive starting structure models were taken from the literature (albite from Williams and Megaw, 1964; dickite from Newnham, 1961; fluorite from Cheetham *et al.*, 1971; muscovite from Güven, 1971; quartz from Young and Post, 1962). Atomic positions and temperature factors were kept constant during the calculations. However, the lattice parameters of all minerals present in

the mixtures, the phase-dependent isotropic line broadening caused by crystallite size effects and microstrain, as well as the zero point deviation, sample displacement, and a background polynomial function of third order were refined in fully automatic mode without a user-defined strategy for refinement. Site occupancies were only refined for the interlayer and octahedral positions of muscovite. In the case of the muscovite-dickite-quartz mixture prepared from the <2 μm muscovite size fraction, application of a *hkl*-dependent line-broadening model (Bergmann and Kleeberg, 1998) was necessary to account for the greater density of stacking faults present in the finely ground mica.

Description of preferred orientation

The most general description of the PO of crystallites in polycrystalline samples is the three-dimensional orientation distribution function. The information required for the construction of this function, however, cannot be obtained from a single angular scan performed in Bragg-Brentano geometry. In the present study, a simplified description of PO is achieved by collecting the XRD patterns on rotated samples, where the orientation of the diffraction vector is fixed in sample coordinates. The PO of mineral grains can, therefore, be effectively described using a two-dimensional PO model.

However, application of such a two-dimensional PO model is only possible in cases where a number of Bragg reflections representing different crystallographic directions have measurable intensities. Step-scan data collected on standard powder mounts used for quantitative phase analysis by the Rietveld method meet this precondition. In contrast, two-dimensional PO description cannot be performed on samples with strong PO and which show only one class of reflections such as oriented clay samples.

In the present contribution, PO description and correction was performed during Rietveld refinement following the method described by Bergmann *et al.* (2001). The algorithm applied is equivalent to models using symmetrized linear combinations of spherical harmonic functions for PO correction (Popa, 1992; Järvinen, 1993; Ferrari and Lutterotti, 1994; Von Dreele, 1997), but it is unique to all Laue classes and orders of the model. Implementation of the algorithm in the Rietveld program BGMN (Bergmann *et al.*, 1998) revealed that the model is numerically robust and can be used conveniently during routine quantitative phase analysis to correct the effects of PO because it forms part of the refinement conducted in fully automatic mode (Bergmann *et al.*, 2001). The only requirement is that the order of the PO correction model must be defined for each component phase prior to the refinement.

The number of parameters refined during Rietveld analysis of the step-scan data depends not only on the order of the PO correction model chosen, but also on the Laue class of the phase under investigation (Bergmann

et al., 2001). Pronounced PO can only be described using higher-order models. However, the choice of a high-order model increases the number of refined parameters drastically, in particular for phases of low symmetry. For reasons of numerical stability, the number of parameters cannot be increased infinitely and a compromise must be found. Table 1 lists the order of the PO correction models chosen in the present study.

Application of the PO correction model during Rietveld refinement yields a list of *hkl*-specific PO correction factors for each component of a multi-phase sample whereby each PO factor represents the relative deviation of the measured intensity of a Bragg reflection from the ideal value representing a random orientation of the crystallites (Bergmann *et al.*, 2001). Thus, the meaning of these factors is comparable to the so-called unit of multiples of random distribution (m.r.d.) widely applied in classical texture analysis. They provide a basis to compare the PO of minerals contained in multi-phase mixtures, but can also be used to evaluate the degree of PO in samples prepared by different techniques. Perfect randomness of crystallites is achieved if the PO correction factors of all *hkl* are unity. Because the Rietveld method represents a full-profile approach

Table 1. Preferred-orientation correction models applied during Rietveld refinement of the artificial mineral mixtures.

Mineral	Laue class	Order of the model	Number of parameters
Albite	$\bar{1}$	4	15
Dickite	$2/m$	2	4
Fluorite	$m\bar{3}m$	6	3
Muscovite	$2/m$	2	4
Quartz	$\bar{3}$	4	5

(all observed *hkl* are taken into account in the PO correction), texture evaluation using this approach is expected to be less sensitive to peak overlap when compared to traditional orientation indices calculated from the intensity ratio of only two Bragg reflections.

The PO correction factors for all *hkl* can also be plotted as a three-dimensional function in crystallographic space (Bergmann *et al.*, 2001). The resultant graph represents the normalized inverse pole figure (with respect to the sample normal), commonly referred to as the normalized polar-axis density in the context of Rietveld refinement. In the present study, these graphs

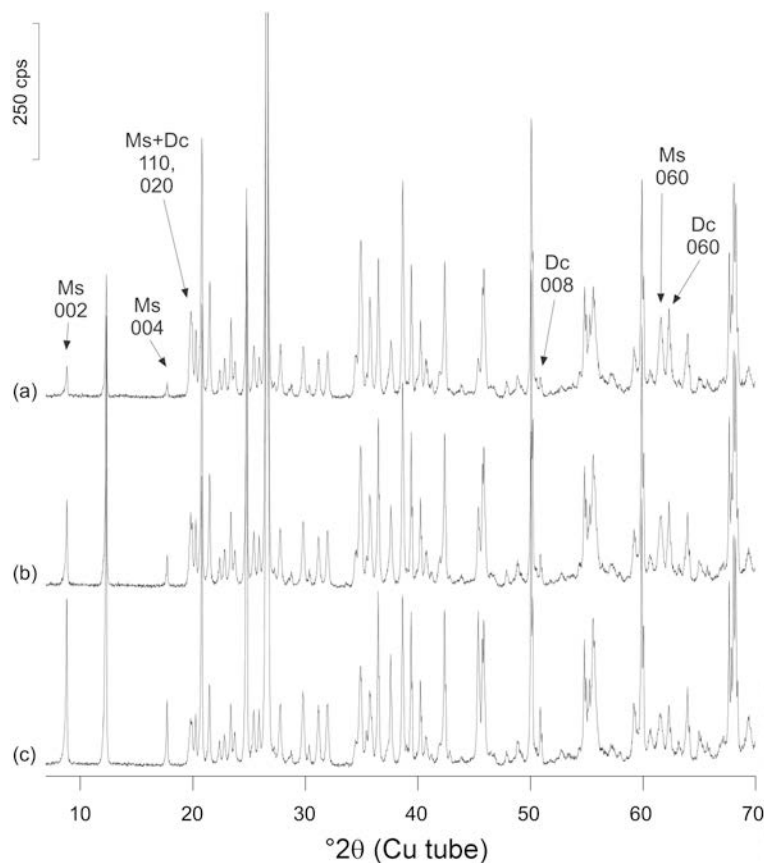


Figure 2. XRD patterns collected on one muscovite-dickite-quartz mixture (the initial particle size of the muscovite component was 2–6.3 μm) prepared by three different sample preparation techniques: (a) spray drying, (b) side loading, and (c) front loading. Abbreviations: Ms = muscovite; Dc = dickite.

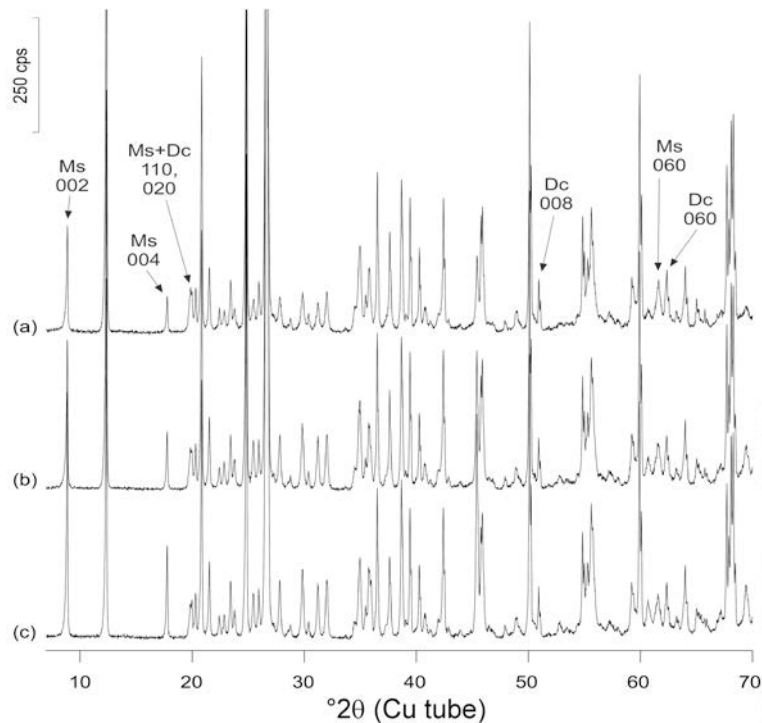


Figure 3. XRD patterns collected on three muscovite-dickite-quartz mixtures prepared by the front-loading technique. The initial particle size of the muscovite component was different in the three mixtures: (a) $<2 \mu\text{m}$ (b) $2\text{--}6.3 \mu\text{m}$ and (c) $6.3\text{--}20 \mu\text{m}$. Abbreviations: Ms = muscovite; Dc = dickite.

were produced from an output file generated by the Rietveld software, BGMN, using the software package MAPLE 6. Inspection of the graphs produced in this way allows rapid qualitative assessment of the calculated PO correction model because maxima will be coincident

with directions normal to the most pronounced crystallite planes showing PO, such as cleavage planes (Bergmann *et al.*, 2001). If crystallites in a sample show a perfectly random orientation, the resultant graph should be a sphere with a radius that is unity.

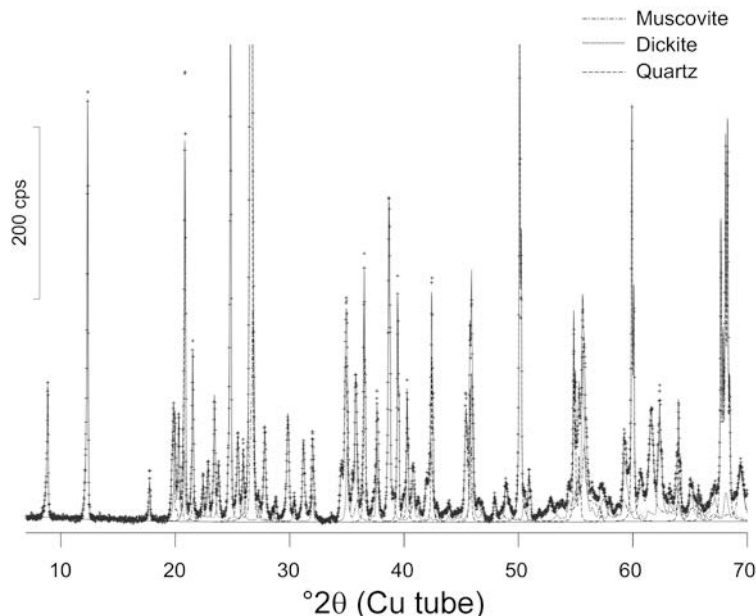


Figure 4. XRD pattern of the muscovite-dickite quartz mixture (initial particle size of the muscovite component was $2\text{--}6.3 \mu\text{m}$) prepared by side loading and profiles simulated for the three components by Rietveld refinement.

RESULTS

Muscovite-dickite-quartz mixture

Initial comparison of the diffraction patterns collected on the muscovite-dickite-quartz mixtures shows that the intensities of the 00 l and 0 k 0 reflections vary significantly between the different sample preparations (Figure 2) suggesting that different degrees of PO were introduced, depending on the method of filling of the sample mounts. The XRD patterns collected on the mixtures containing muscovite of different primary particle size also exhibit variations in the relative peak intensities, at least for the 00 l peaks of muscovite contained in front- and side-loaded samples (Figure 3). This observation implies that, despite fine grinding in the McCrone micronizing mill, PO varies as a function of the initial particle size of the constituent phases.

Despite the effects caused by the PO of the particles, the Rietveld refinement of the XRD patterns yielded simulated patterns that are in good agreement with the measured step-scan data. The intensities of the basal reflections were described correctly (Figure 4), suggesting that PO in standard powder mounts can be modeled satisfactorily by the correction algorithm applied. Furthermore, the results of quantification agree well with the true composition of the artificial mixtures (Table 2). However, independent of the sample-preparation technique used, a slight tendency for underestimating the relative proportion of quartz and overestimating the relative dickite content was noted. This minor systematic error may be related to the incorrectness of one of the starting structure models and/or slightly inadequate modeling of the peak shapes.

As expected, the shapes of the calculated normalized polar-axis densities of muscovite and dickite contained in the various sample mixtures are strongly influenced by the platy nature of the clay mineral flakes (Figures 5, 6). Their maxima coincide with c^* , which is perpendicular to the cleavage plane, whereas minimum values correspond to the $[hk0]$ zone. All shapes are rotationally symmetrical in the a - b plane, suggesting that the muscovite and dickite platelets have irregular contours after grinding.

Visual inspection of the shapes of the normalized polar-axis densities of muscovite and dickite contained in the artificial mixtures highlights the fact that the degree of PO depends primarily on the filling technique (Figure 5). Conventional front-loading of the samples yielded the most pronounced PO of the clay particles. Although the degree of PO for both platy monoclinic sheet silicates may coincidentally have the same magnitude (Figure 5), this is unlikely to occur if the minerals are of different particle size. Indeed, the differences in primary particle size of the muscovite were preserved during the milling procedure (Figure 6). The PO of muscovite in the side-loaded samples is least pronounced for the sample prepared from the $<2\ \mu\text{m}$ fraction, but increases significantly for the coarser

Table 2. Results of the Rietveld quantitative phase analysis (wt.% \pm 3 σ) of the muscovite-dickite-quartz mixtures prepared using different initial particle sizes of the muscovite component and methods of sample preparation.

Mineral	Mixture with an initial muscovite particle size of $<2\ \mu\text{m}$		Mixture with an initial muscovite particle size of $2\text{--}6.3\ \mu\text{m}$		Mixture with an initial muscovite particle size of $6.3\text{--}20\ \mu\text{m}$	
	Front-loading	Spray-drying	Front-loading	Spray-drying	Front-loading	Spray-drying
Muscovite	31.9 \pm 0.9	28.2 \pm 0.8	30.6 \pm 0.6	29.5 \pm 0.6	30.5 \pm 0.6	31.5 \pm 0.6
Dickite	29.6 \pm 0.7	31.2 \pm 0.6	30.4 \pm 0.6	31.0 \pm 0.6	30.8 \pm 0.6	30.5 \pm 0.6
Quartz	38.5 \pm 0.7	40.6 \pm 0.6	39.0 \pm 0.6	39.5 \pm 0.6	38.7 \pm 0.6	38.0 \pm 0.6

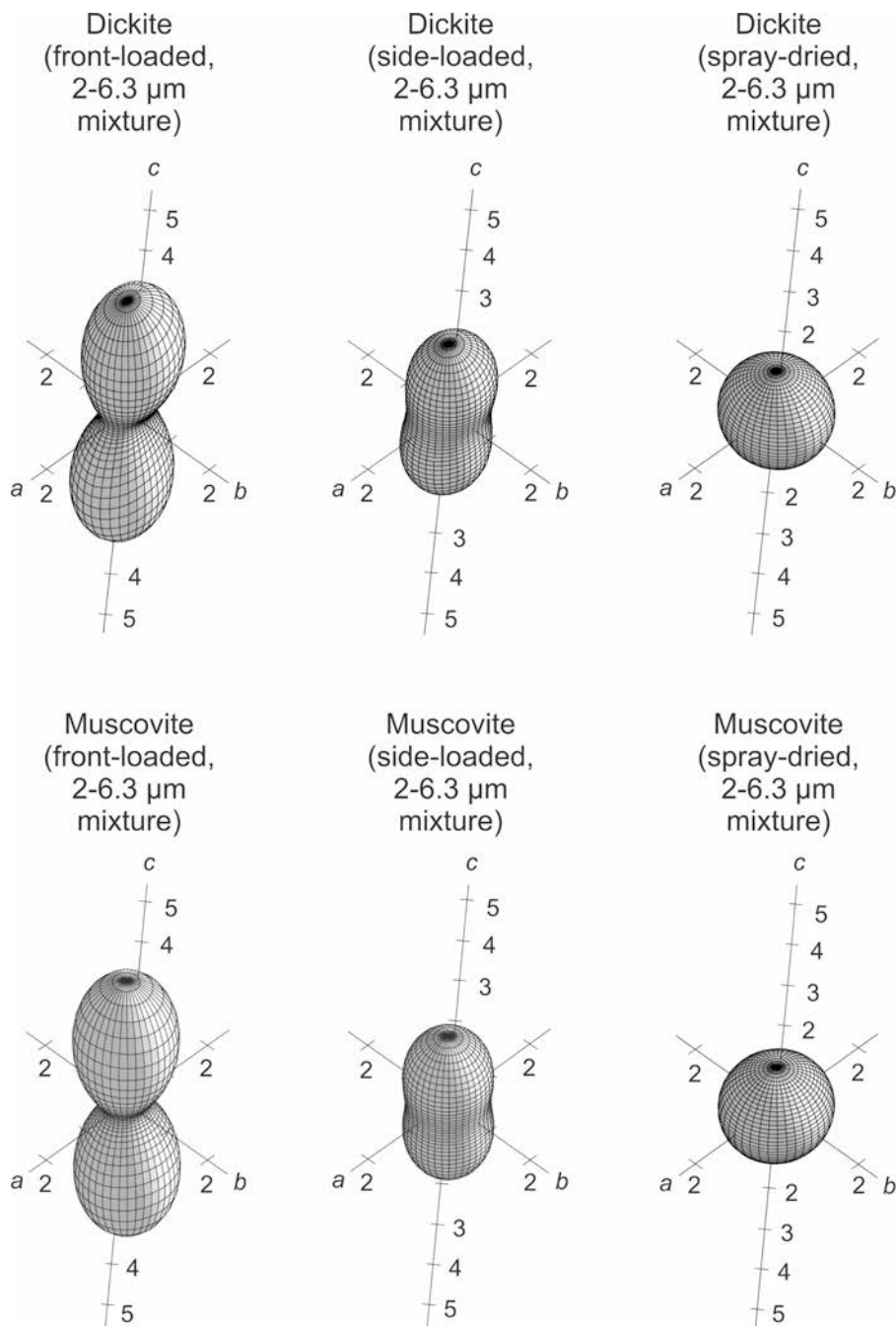


Figure 5. Shapes of the normalized polar-axis densities of muscovite and dickite in one muscovite-dickite-quartz mixture (initial particle size of the muscovite component was 2–6.3 μm) prepared by different sample-preparation techniques.

fractions. In contrast, the PO of dickite is similar for all three of the different side-loaded samples.

Close inspection of the PO correction factors calculated for the front- and side-loaded samples (Table 3) shows the relevance of the correction of the intensities for the $00l$ reflections as well as for the $0k0$ peaks, which are often used for clay mineral quantification by single-line methods (Środoń, 2002). In the extreme case of the front-loaded sample prepared from

the coarse-grained muscovite starting material, the relative intensities of these peaks deviate by a factor of 4.71 from randomness. Even in the case of dickite contained in the side-loaded samples, the intensities of the $0k0$ reflections were noted to be ~25% less (correction factors of 0.69 to 0.76) than in a truly random sample (Table 3). The best result using side-loaded mounts was obviously obtained for the mixture containing muscovite that had a primary particle size of

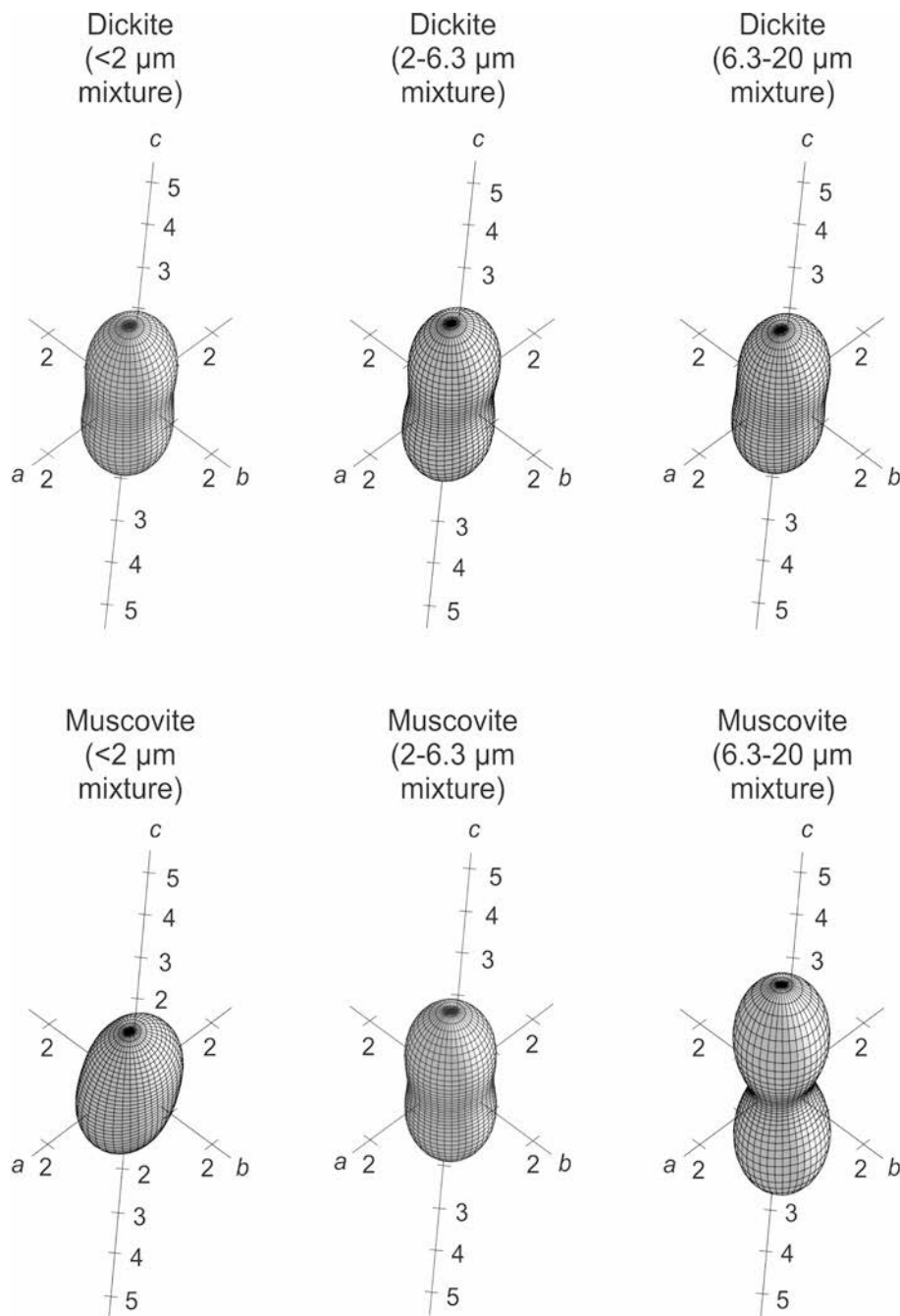


Figure 6. Shapes of the normalized polar-axis densities of muscovite and dickite in three muscovite-dickite-quartz mixtures prepared by the side-loading technique. The initial particle sizes of the muscovite component were different in the three mixtures.

$<2\ \mu\text{m}$. However, the intensities of the $00l$ peaks still deviate by a factor of 1.13 from those of a perfectly random sample. This observation highlights the significant errors that may occur if quantitative phase analysis is performed using single-line intensities, even if the side-loading technique is applied.

As expected, the spray-dried samples were found to be completely random. The calculated PO correction factors are close to unity and no relationship between the

shapes of the normalized polar-axis densities and the initial particle size of the muscovite component was observed (Table 3). This observation is in agreement with the commonly held perception that spray-dried clay samples are random.

Fluorite-albite-quartz mixture

Rietveld refinement of the XRD patterns collected on the fluorite-albite-quartz mixture shows that PO of non-

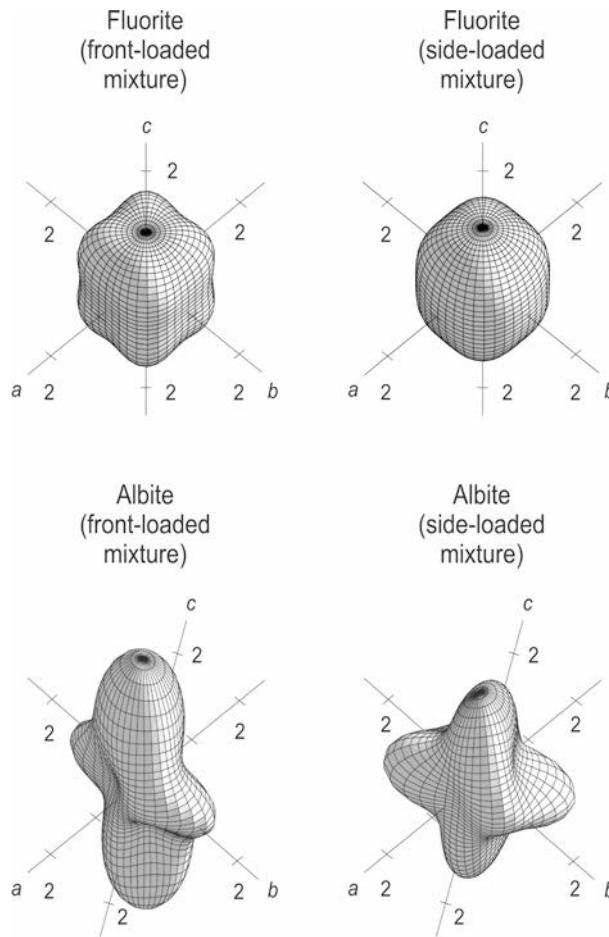


Figure 7. Shapes of the normalized polar-axis densities of fluorite and albite in the fluorite-albite-quartz mixture prepared by different sample-preparation techniques.

clay minerals having one or multiple cleavages is significant if conventional sample preparation techniques involving front- or side-loading of the powders are used (Figure 7).

The occurrence of PO in the front- and side-loaded samples is highlighted by the shapes of the normalized polar-axis densities of fluorite and albite (Figure 7). A strong texture-induced over-representation was observed for the intense 111 fluorite line, with PO correction

factors of 1.16 and 1.08 for the front- and side-loaded preparations, respectively. Albite contained in the same preparations also shows a pronounced PO, which is related to the perfect {001} and {010} cleavages of this triclinic mineral (Figure 7). The front-loaded preparation, with a high-order PO correction model applied (Table 1), yielded PO correction factors of 1.98 for the 002 reflection and of 1.37 for the 040 albite peak. Preferred orientation of albite particles was less

Table 3. Preferred orientation correction factors (I_{obs}/I_{id}) for selected classes of Bragg reflections of muscovite and dickite contained in muscovite-dickite-quartz mixtures prepared using different initial particle sizes of the muscovite component and methods of sample preparation (I_{obs} = observed intensity, I_{id} = ideal intensity in a random sample).

Preparation	Mixture with an initial muscovite particle size of <2 μm				Mixture with an initial muscovite particle size of 2–6.3 μm				Mixture with an initial muscovite particle size of 6.3–20 μm			
	Muscovite		Dickite		Muscovite		Dickite		Muscovite		Dickite	
	I_{obs}/I_{id} 00l	I_{obs}/I_{id} 0k0	I_{obs}/I_{id} 00l	I_{obs}/I_{id} 0k0	I_{obs}/I_{id} 00l	I_{obs}/I_{id} 0k0	I_{obs}/I_{id} 00l	I_{obs}/I_{id} 0k0	I_{obs}/I_{id} 00l	I_{obs}/I_{id} 0k0	I_{obs}/I_{id} 00l	I_{obs}/I_{id} 0k0
Front-loading	1.94	0.51	3.18	0.33	3.03	0.40	2.74	0.39	4.71	0.20	2.52	0.45
Side-loading	1.13	0.92	1.57	0.75	1.64	0.74	1.67	0.69	2.35	0.53	1.50	0.76
Spray-drying	1.02	1.01	0.99	1.03	0.97	1.01	0.97	1.04	1.00	1.00	1.00	1.04

Table 4. Results of the Rietveld quantitative phase analysis (wt.% \pm 3 σ) of the albite-fluorite-quartz mixtures using different methods of sample preparation.

Mineral	Front-loading	Side-loading
Albite	29.2 \pm 0.6	28.4 \pm 0.6
Fluorite	29.4 \pm 0.4	30.0 \pm 0.4
Quartz	41.4 \pm 0.5	41.7 \pm 0.5

pronounced in the side-loaded sample with calculated PO correction factors of 1.62 and 1.37 for the 002 and 040 albite reflections, respectively.

The observed variations in the shapes of the normalized polar-axis densities within the albite *a-b* plane (Figure 7) indicate that parameter correlation of the high-order PO correction model occurred during Rietveld refinement, presumably due to the extensive overlap of the intense *0k0* and *hk0* plagioclase reflections. This problem could not be overcome by the application of the lower-order PO correction model because texture-induced deviations from the ideal peak intensities could not be described adequately in this way. However, the mineral contents calculated by Rietveld refinement were close to the true composition of the mixture for both front- and side-loaded samples (Table 4).

DISCUSSION AND CONCLUSIONS

The results of the present study highlight the fact that PO of particles in standard XRD powder samples prepared from, for example, clay- or mica-bearing sediments or sedimentary rocks, cannot be completely avoided if the samples are ground in a McCrone micronizing mill and mounted in front- or side-loading holders. Application of these standard techniques, which are common in laboratories worldwide, precludes precise and accurate quantitative phase analysis unless PO correction is performed during subsequent quantification.

Spray drying probably represents the only effective procedure to prepare perfectly random powder mounts, and measurements on samples prepared by this technique can be evaluated by any quantification method without the need for PO correction. If spray drying cannot be conducted due to the presence of unstable minerals or for other reasons, including lack of equipment or problems with the mechanical stability of the samples in conventional diffractometer settings, side-loading of the samples may be the best choice to reach an acceptable level of randomness. However, because side-loading invariably introduces a certain degree of PO, which will generally vary for the different minerals contained in multi-phase samples, PO correction models must still be applied during phase quantification. The PO corrections must be carried out

independently for each constituent phase because minerals of similar crystal habit may show different degrees of PO within a single sample, as demonstrated herein.

The systematic experiments carried out during this study show that application of the PO correction model developed by Bergmann *et al.* (2001) was successful. No systematic differences in the quantitative XRD data were observed for the different preparation techniques and the calculated mineral proportions generally conform well to the true composition of the artificial mixtures. Based on the results from the present study, models using symmetrized spherical harmonics expansions or similar approaches are suggested to be most appropriate to perform this task in quantitative Rietveld phase analysis because they are able to correct the PO of axially symmetric flat-plate minerals, but also of non-clay phases that are often characterized by one or multiple cleavages.

ACKNOWLEDGMENTS

The authors are grateful to J. Bergmann for implementing an output feature in the Rietveld program BGMN allowing the export of the tensor elements used for the construction of normalized polar-axis densities. Careful reviews by O. Omotoso and an anonymous reviewer helped to improve an earlier version of the manuscript. The authors thank U. Kempe for conducting the SEM investigations on the dickite sample. The paper benefited from numerous discussions with colleagues including J. Środoń, D. Eberl, O. Omotoso and M. Plötze who shared their personal experiences in preparing random powder samples with us. SH acknowledges the support of the Scottish Executive Environment and Rural Affairs Department.

REFERENCES

- Bergmann, J. and Kleeberg, R. (1998) Rietveld analysis of disordered layer silicates. *Materials Science Forum*, **278–281**, 300–305.
- Bergmann, J., Friedel, P., and Kleeberg, R. (1998) BGMN – a new fundamental parameters based Rietveld program for laboratory X-ray sources, its use in quantitative analysis and structure investigations. *Commission of Powder Diffraction, International Union of Crystallography CPD Newsletter*, **20**, 5–8.
- Bergmann, J., Monecke, T., and Kleeberg, R. (2001) Alternative algorithm for the correction of preferred orientation in Rietveld analysis. *Journal of Applied Crystallography*, **34**, 16–19.
- Bish, D.L. and Reynolds, R.C., Jr. (1989) Sample preparation for X-ray diffraction. Pp. 73–99 in: *Modern Powder Diffraction* (D.L. Bish and J.E. Post, editors). Reviews in Mineralogy, **20**. Mineralogical Society of America, Washington, D.C.
- Blount, A.M. and Vassiliou, A.H. (1979) A new method of reducing preferred orientation in diffractometer samples. *American Mineralogist*, **64**, 922–924.
- Brindley, G.W. and Kurtosy, S.S. (1961) Quantitative determination of kaolinite by X-ray diffraction. *American Mineralogist*, **46**, 1205–1215.
- Cheetham, A.K., Fender, B.E.F., and Cooper, M.J. (1971) Defect structure of calcium fluoride containing excess

- anions: I. Bragg scattering. *Journal of Physics C*, **4**, 3107–3121.
- Dermatas, D., Chrysochoou, M., Pardali, S., and Grubb, D.G. (2007) Influence of X-ray diffraction sample preparation on quantitative mineralogy: Implications for chromate waste treatment. *Journal of Environmental Quality*, **36**, 487–497.
- v. Engelhardt, W. (1955) Über die Möglichkeit der quantitativen Phasenanalyse von Tonen mit Röntgenstrahlen. *Zeitschrift für Kristallographie*, **106**, 430–459.
- Ferrari, M. and Lutterotti, L. (1994) Method for the simultaneous determination of anisotropic residual stresses and texture by X-ray diffraction. *Journal of Applied Physics*, **76**, 7246–7255.
- Flörke, O.W. and Saalfeld, H. (1955) Ein Verfahren zur Herstellung texturfreier Röntgen-Pulverpräparate. *Zeitschrift für Kristallographie*, **106**, 460–466.
- Güven, N. (1971) The crystal structures of $2M_1$ phengite and $2M_1$ muscovite. *Zeitschrift für Kristallographie*, **134**, 196–212.
- Hillier, S. (1999) Use of an air brush to spray dry samples for X-ray powder diffraction. *Clay Minerals*, **34**, 127–135.
- Hillier, S. (2003) *Quantitative analysis of clay and other minerals in sandstones by X-ray powder diffraction (XRPD)*. Special Publication of the International Association of Sedimentologists, **34**, 213–251.
- Hughes, R. and Bohor, B. (1970) Random clay powders prepared by spray-drying. *American Mineralogist*, **55**, 1780–1786.
- Järvinen, M. (1993) Application of symmetrized harmonics expansion to correction of the preferred orientation effect. *Journal of Applied Crystallography*, **26**, 525–531.
- Klug, H.P. and Alexander, L.E. (1954) *X-ray diffraction procedures for polycrystalline and amorphous materials*. John Wiley & Sons, New York, 716 pp.
- Monecke, T., Köhler, S., Kleeberg, R., Herzig, P.M., and Gemmel, J.B. (2001) Quantitative phase-analysis by the Rietveld method using X-ray powder-diffraction data: Application to the study of alteration halos associated with volcanic-rock-hosted massive sulfide deposits. *The Canadian Mineralogist*, **39**, 1617–1633.
- Moore, D.M. and Reynolds, R.C., Jr. (1997) *X-ray Diffraction and the Identification and Analysis of Clay Minerals*, 2nd edition, Oxford University Press, New York.
- Newnham, R.E. (1961) A refinement of the dickite structure and some remarks on polymorphism in kaolin minerals. *Mineralogical Magazine*, **32**, 683–704.
- O'Connor, B.H. and Chang, W.J. (1986) The amorphous character and particle size distributions of powders produced with the micronizing mill for quantitative X-ray powder diffractometry. *X-ray Spectrometry*, **15**, 267–270.
- Popa, N.C. (1992) Texture in Rietveld refinement. *Journal of Applied Crystallography*, **25**, 611–616.
- Reynolds, R.C., Jr. (1986) The Lorentz-Polarization factor and preferred orientation in oriented clay aggregates. *Clays and Clay Minerals*, **34**, 359–367.
- Reynolds, R.C., Jr. (1989) Principles and techniques of quantitative analysis of clay minerals by X-ray powder diffraction. Pp. 4–36 in: *Quantitative Mineral Analysis of Clays* (D.R. Pevear and F.A. Mumpton, editors). CMS workshop lectures **1**, The Clay Minerals Society, Bloomington, Indiana.
- Šrodoň, J. (2002) Quantitative mineralogy of sedimentary rocks with emphasis on clays and with applications to K-Ar dating. *Mineralogical Magazine*, **66**, 677–687.
- Šrodoň, J. (2006) Identification and quantitative analysis of clay minerals. Pp. 765–787 in: *Handbook of Clay Science* (F. Bergaya, B.K.G. Theng, and G. Lagaly, editors). Developments in Clay Science, **1**, Elsevier, Amsterdam.
- Šrodoň, J., Drits, V.A., McCarty, D.K., Hsieh, J.C.C., and Eberl, D.D. (2001) Quantitative X-ray diffraction analysis of clay-bearing rocks from random preparations. *Clays and Clay Minerals*, **49**, 514–528.
- Taylor, R.M. and Norrish, K. (1966) The measurement of orientation distribution and its application to quantitative X-ray diffraction analysis. *Clay Minerals*, **6**, 127–142.
- Von Dreele, R.B. (1997) Quantitative texture analysis by Rietveld refinement. *Journal of Applied Crystallography*, **30**, 517–525.
- Williams, P.P. and Megaw, H.D. (1964) The crystal structures of low and high albites at -180°C . *Acta Crystallographica*, **17**, 882–890.
- Young, R.A. and Post, B. (1962) Electron density and thermal effects in alpha quartz. *Acta Crystallographica*, **15**, 337–346.
- Zevin, L. and Viaene, W. (1990) Impact of clay particle orientation on quantitative clay diffractometry. *Clay Minerals*, **25**, 401–418.
- Zhang, G., Germaine, J.T., Martin, R.T., and Whittle, A.J. (2003) A simple sample-mounting method for random powder X-ray diffraction. *Clays and Clay Minerals*, **51**, 218–225.

(Received 3 August 2007; revised 6 May 2008; Ms. 0053; A.E. B. Lanson)