XRD-based quantitative analysis of clay minerals using reference intensity ratios, mineral intensity factors, Rietveld, and full pattern summation methods: A critical review

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Abstract

The quantification of clay minerals is essential for the evaluation of clay-rich rock and soil, but it remains challenging due to the unique structures and various element compositions of clay minerals. In this article, several quantification methods for clay minerals sourced from X-ray diffraction (XRD) analysis, mainly recommending the reference intensity ratio (RIR), mineral intensity factor (MIF), Rietveld, and full pattern summation methods are reviewed. Principles and applications of these methods are focused upon in addition to related differences in the analysis of clay minerals (i.e., sample preparation, the selection of characteristic reflections for quantification and standards added during analysis). This critical review also provides a proposal for selection of an adaptive XRD quantification method to be applied to various clay-rich samples. Copyright © 2018, Guangzhou Institute of Geochemistry. Production and hosting by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

Keywords: XRD; Quantitative analysis; Clay minerals; RIR and MIF methods; Rietveld and full pattern summation methods

1. Introduction

Over the past century, X-ray diffraction (XRD) has gradually became one of the most important analytical approaches used in the qualitative and quantitative study of geological samples (Ross and Kerr, 1931; Gruner, 1934, 1939, 1935a, b; Clark and Reynolds, 1936; Nagelschmidt, 1938; Bradley, 1940; Alexander and Klug, 1948; Taylor, 1978; Bish and Howard, 1988; Bish, 1994; Środoń, 2002; Chipera and Bish, 2013). Many important theoretical works have been published for the application of qualitative and quantitative work (Clark and Smith, 1936; Alexander and Klug, 1948; Chung, 1974, 1975; Brindley, 1980; Chipera and Bish, 2013). XRD analysis is believed to be the most suitable method for routine quantitative analysis compared to any other single technique, such as Fourier transform infrared spectroscopy (FTIR), chemical analysis and electron microscopy (Bish and Post, 1993; Mumme et al., 1996). However, the quantitative analysis of certain minerals and especially of clay minerals remains as a major challenge due to the various chemical compositions, preferred orientation, structural disorder and great structural diversity of clay minerals (Zwell and Danko, 1975; Brindley, 1980; Moore and Reynolds, 1997; Hillier, 2000; Środoń et al., 2001; Środoń, 2002, 2013; Bergaya and Lagaly, 2006).

Clay minerals are important components of soil and sedimentary rocks. For example, the quantity of clay minerals is up to approximately 35 wt. % of sedimentary rocks (Garrels and Mackenzie, 1971). Clay minerals have been confirmed to affect the properties of soils and rocks because they possess

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Peer review under responsibility of Guangzhou Institute of Geochemistry.

unique structures and surface properties, such as swelling (Moore and Reynolds, 1997; Yuan et al., 2008, 2009; Fan et al., 2009), cation exchange capacity (Środoń and McCarty, 2008; Yuan et al., 2009, 2013; He et al., 2010) and solid acidity (Okada et al., 2006; Liu et al., 2011; 2013a [1], b, c, d, e). They are also "recorders" of geological processes (e.g., weathering, transportation, sedimentation, and diagenesis) and can provide abundant information on soil or rock trans- formations (Griffin et al., 1968; Rateev et al., 1969; Jacobs and Hays, 1972; Singer, 1984; Środoń, 2002, 2013). The identifi- cation of essential information on mineralogical properties and geological processes is affected by quantitative analysis of clay mineral compositions (Środoń, 2002). For example, the adsorption of methane in the hydrocarbon source rock of a reservoir is strongly related to the amount of clay minerals (Ji et al., 2012; Liu et al., 2013b, d [2]). In this case, it is of great significance to obtain clay mineral compositions of soil and sedimentary rocks for researching the source mineralogy (Środoń et al., 2006).

Clay minerals denote phyllosilicate minerals and minerals which impart plasticity to clay and which harden upon drying or firing (Guggenheim and Martin, 1995; Bergaya and Lagaly, 2006). These minerals usually exhibit platy morphology and (001) cleavage (Moore and Reynolds, 1997). In addition, they can be described as the construction of two parts: a sheet of corner-linked tetrahedral structure (T) and a sheet of edge- linked octahedral structure (O), which may connect in either a 1:1 or 2:1 combination to form an anisotropic TO or TOT plane (Moore and Reynolds, 1997; Bergaya and Lagaly, 2006).

However, the quantification of clay minerals remains complex relative to the quantification of other minerals as clay minerals have unique structures, such as various polytypes and types of defects, and can vary in chemical composition and in terms of effects of preferred orientation (Środoń, 2002). Such challenges mainly derive from the clay mineral characteristics cited below:

1) Variable chemical composition: i) isomorphous substitu- tion occurring in T sheet and O sheet (i.e., in montmo- rillonite and illite, Si^{4+} in the T sheet is usually replaced with Al^{3+}, and Al^{3+} in the O sheet is replaced with Mg^{2+}, Fe^{2+}) diversifies the XRD patterns of clay minerals (Środoń and McCarty, 2008); ii) the interlayer cations of some clay minerals, such as Ca^{2+} or Na^+ in the interlayer space of montmorillonite, affect the position of charac- teristic reflections of clay minerals during quantification (Mooney et al., 1952; Liu et al., 2013a, c [3]).
2) Variable structures: highly variable structures involving different types of layer interstratification (e.g., illite-smectite mixed-layer minerals) and various defects that damage the three dimensional periodicity usually exist in clay minerals (Drits et al., 1994; Środoń et al., 2001; Viennet et al., 2015). Due to disturbed three-dimensional periodicity, XRD pat- terns of clay minerals are more complicated than the patterns of materials with higher degrees of crystallinity (Brindley, 1980; Środoń, 2002, 2013).
3) Preferred orientation: the orientation of clay mineral par- ticles affects the XRD intensities of powdered samples. The measurement of accurate XRD reflection intensity is based on a random orientation sample. However, most clay mineral particles exhibit platy characteristics and typically preparation methods such as front-loading often produce preferred orientation of clay minerals (Hillier, 1999). The XRD reflection intensities of clay minerals are usually enhanced by the preferred orientation (Lippmann, 1970) and thus the preferred orientation is believed to be a major source of error in quantitative analysis of clays minerals (Środoń et al., 2001). Therefore, preferred orientation ef- fects on the quantification of clay minerals should be minimized through the use of certain methods (Brindley, 1980; Moore and Reynolds, 1997).

Moreover, water adsorbed in the interlayer spaces of some clay minerals usually interferes with quantitative evaluations. For example, when saturated with water molecules, Ca- montmorillonite (the interlayer cation is Ca^{2+}) contains two planes of water molecules in the interlayer space and shows a d_{001} value of approximately 1.50 nm, and Na-montmorillonite (the interlayer cation is Na^+) has one plane of water molecules with a d_{001} value of approximately 1.24 nm (Gruner, 1935a; Bergaya and Lagaly, 2006). Thus, interlayer water molecules greatly affect the (001) XRD reflections of clay minerals and further interrupt the quantitative analysis process.

These abovementioned characteristics lead to considerable differences in information (i.e., intensities and positions of reflections) on XRD reflections between different samples of the same clay mineral. In addition, large analytical errors in quantification can result when analyzing these variable pat- terns of XRD reflections when inappropriate quantification reflections are chosen (Środoń et al., 2001).

On the other hand, the accuracy of quantitative analysis is, as commonly known, strongly dependent on the samples preparing methods and XRD instrument conditions (Alexander and Klug, 1948; Bish and Reynolds, 1989; Moore and Reynolds, 1997; Hurst et al., 1997; Hillier, 1999; Środoń et al., 2001). For the former, two aspects are believed to be the most important: sample grinding and the preparation of pow- der mounts. During the fine grinding of the samples, grinding methods and the according time should be carefully consid- ered to satisfy requirement of the particle size (at least <20 μm (Środoń et al., 2001), details see, Supporting Information, Section 1.2.1). Moreover, two kinds of XRD sample loading methods are used (front-loading and side-loading) for prepa- ration of powder mounts (details see, Supporting Information, Section 1.2.2). For the latter, XRD instrument conditions should also be carefully considered (e.g., power settings, counting time and step size, width of slits, and length of the irradiated sample). For example, longer counting time is

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[1] The authors of this reference refer to Liu D. et al.
[2] The authors of this reference refer to Liu D. et al.
[3] The authors of this reference refer to Liu H. et al.

needed to get the accurate intensity data (for details, see Supporting Information, Section 1.1).

Several quantitative methods based on XRD analyses for clay mineral quantification have been developed (e.g., the reference intensity ratio (RIR) method (Visser and de Wolff, 1964), the mineral intensity factor (MIF) method (Moore and Reynolds, 1997), the external standard method (Leroux et al., 1953), the no-standard method (Salyn and Drits, 1972), the Rietveld method (Rietveld, 1969), and the full pattern summation method (Chipera and Bish, 2013)). These methods are divided into two categories (single reflection methods and whole pattern methods) on the basis of simple criteria on the ways of measuring XRD reflection and different standards. The first group of approaches, single reflection methods, is dependent on the choice of an individual reflection as a quantification reflection of the mineral weight percentage and a natural sample (e.g., corundum (Chung, 1974; Hubbard and Snyder, 1988; Hillier, 1999)) as a standard; the second group, whole pattern methods, is based on using the intensities of compositions of a mixture by matching the whole XRD pattern of a sample with the pattern of standards. Whole pattern methods can be further subdivided into two techniques: i) when the patterns of standards are obtained from natural minerals, the method can be referred to as a whole pattern/ natural standard method; ii) when the diffraction patterns of standards are generated from crystallographic data, the method can be referred to as a whole pattern/computed standard method (Taylor, 1991; Taylor and Rui, 1992; Środoń, 2013).

The most widely used single reflection and whole pattern methods are reviewed in this paper. The principles and applications of these methods are explored in addition to differences in the analysis of clay minerals. Moreover, we propose the use of an adaptive approach to the XRD quantitative analysis of clay minerals.

2. Single reflection methods and whole pattern methods

2.1. Single reflection methods

An individual characteristic reflection is used in the single reflection method for the quantitative analysis of clay minerals. According to how standards are used (few researchers quantify clay mineral content without using a standard; for conciseness, the no-standard method is not described in this review), two groups are identified: i) the internal standard method whereby extra standards are added to samples during XRD measurement and ii) the external standard method, in which standards are used but not added to samples during XRD measurement. However, the external standard method is seldom used in quantifying clay minerals; to the best of our knowledge, only Engelhardt (1955) has used this method to quantify the components of fine clay mineral powder. The present review focuses on the internal standard method.

In quantitative X-ray diffraction analysis of clay minerals, analysis accuracy is affected by the matrix effect arising from the unique structures of clay minerals.

Theoretically, this matrix effect can be described as follows:

It is known that the intensity of X-ray diffraction by a component P (I_p) in a mixture can be expressed by the following equation (Alexander and Klug, 1948):

$$Ip = K_p w_p / \overline{\mu} \tag{1}$$

where w_p is the mass % of component P in the mixture; K_p is a constant that is dependent on the nature of component P, and $\overline{\mu}$ is the average mass attenuation coefficient, which is a constant in a single phase material. Therefore, the intensity of this single phase displays a linear relationship with the X-ray diffracted volume of the single phase material sample. However, for a multiphase mineral sample, some minerals strongly adsorb X-rays (Leroux et al., 1953), and then this linear relationship between the phase X-ray diffraction intensity and phase concentrations does not exist. This phenomenon is referred to as the matrix effect.

To eliminate the matrix effect, internal standard methods, which are widely used for mixture analysis by X-ray diffraction, are applied. The first application of internal standard method was reported by Clark and Reynolds (1936) for the quantitative analysis of mine dust. Alexander and Klug (1948) theoretically described the internal standard method. The formula developed by Alexander and Klug is as follows (Alexander and Klug, 1948):

$$x_p = kI_p / I_s \tag{2}$$

where k is a coefficient related to the nature of component P and internal standard s, to properties of the X-ray diffraction test (i.e., the geometry of the apparatus and the wavelength of the X-ray) and to the amount added from the standard. x_p is the mass % of component P. I_p and I_s are the X-ray diffraction intensities of component P and the standard s, respectively.

Common internal standards are LiF (Carter et al., 1987), α-Al_2O_3 (Hubbard and Snyder, 1988), and AlO(OH) (Gibbs, 1967), and these standards usually have low attenuation coefficients, preferably only a few XRD reflections and at least one conveniently located strong reflection (Brindley, 1980). When an internal standard is added, experimental conditions generally become the same for the sample and standard. The I_p/I_s value does not change with different sample compositions and under different experimental conditions, and thus the influence of matrix effect disappears.

Traditionally, two types of internal standard minerals, corundum (α-Al_2O_3) and zincite (ZnO) are applied to quantify clay-rich samples. For example, Hillier (2000) used α-Al_2O_3 as an internal standard in a sandstone sample quantitative analysis, and Środoń et al. (2001) applied ZnO as an internal standard for clay-bearing rock sample quantification. These two quantitative methods are known as the RIR (Moore and Reynolds, 1997) and MIF methods (Środoń et al., 2001) and they typically use α-Al_2O_3 and ZnO as standards, respectively.

2.1.1. The RIR method

Visser and de Wolff (1964) proposed that the Joint Committee on Powder Diffraction Standards (JCPDS) should apply α-Al$_2$O$_3$ as the standard for comparing the diffraction intensities of powder materials, which was permitted by JCPDS. Since then, the RIR method has been widely applied for the quantification of clay minerals in soil and rocks while using pure α-Al$_2$O$_3$ (which is highly stable and widely available) as an internal standard. For example, Van der Marel (1966) used the RIR method to conduct a quantitative analysis of clay minerals from soils.

However, during the applications of RIR method, problems related to the quantification of clay minerals appeared during sample preparation as a result of well and perfectly oriented structural arrangements of clay minerals. To solve this problem, Quakernaat (1970) developed a simple technique for preparing clay mineral samples that involves using a suction-on-membrane filter to improve the sample preparation procedure for the RIR method. According to tests on clay mineral mixtures, quantitative determinations of kaolinite, smectite and illite in relatively complex systems were found to be accurate with the errors controlled to less than 7%; for chlorite, vermiculite and pyrophyllite, the error was held at less than 10% (Quakernaat, 1970).

Four years later, Chung (1974) found that processes of the RIR method are rather tedious since a calibration curve is needed for each component sought; each calibration curve requires at least three standards, and each standard must contain exactly the same percentage of pure reference material chosen. Therefore, he proposed a new way of acquiring slopes k for any binary system, and the formula for the quantitative analysis of multi-component systems is presented as follows:

$$X_1 = 1 \left/ \left(1 + \frac{k_1 I_2}{k_2 I_1}\right) \right. \tag{3}$$

where X_1 is the weight fraction of component 1; k_1 and k_2 are the reference intensity ratios of components 1 and 2, respectively; and I_1 and I_2 are the intensities of X-rays diffracted by a selected reflection of components 1 and 2, respectively. According to this formula, the quantitative composition of a binary system can be easily calculated from the intensity ratio of the strongest diffraction scan. Mathematically, equation 3 represents a straight line passing through the origin with a slope $k = k_1/k_2$ when I_1/I_2 is plotted against X_1/X_2.

Simply, the RIR value is calculated from the following equation (Hillier, 2000):

$$RIR_{i,s} = \left(\frac{X_s}{X_i}\right) \left(\frac{I_{(hkl)i}}{I_{(hkl)'_s}}\right) \left(\frac{I^{rel}_{(hkl)'_s}}{I^{rel}_{(hkl)i}}\right) \tag{4}$$

where X is the weight fraction of the tested samples; I is the intensity of the characteristic reflection; I^{rel} is the relative intensity of the reflection; and i and s are the clay mineral sample and internal standard phase s, respectively.

When corundum is chosen as an internal standard, $RIR_{i,s}$ values are known as I/I_{cor} or RIR_{cor} ('cor' is denoted as the 'corundum') (Hubbard and Snyder, 1988; Hillier, 2000). To obtain the RIR_{cor} value, a binary system composed of a corundum and a clay mineral is prepared, and the mass ratio of the corundum and clay mineral is 1:1. The RIR_{cor} value is then determined based on the intensities of the most intense corundum reflection ($I_{(113)cor}$) and clay mineral reflection ($I_{(hkl)i}$).

After the calculation of RIR_{cor}, the concentration of any phase i in a sample spiked with a known amount of corundum is given by Hillier (2000):

$$X_i = \left(\frac{X_{cor}}{RIR_{cor}}\right) \left(\frac{I_{(hkl)i}}{I_{(113)cor}}\right) \tag{5}$$

To accommodate for significant chemical or preferred orientation effects that distort observed intensities from true intensities of XRD reflections in the quantification of clay minerals *via* the Chung-improved RIR method, Chipera and Bish (1995) further improved Chung's method by using the intensity ratios from two non-parallel reflections. The effects of preferred orientation were in turn minimized by using these two non-parallel reflections with only ±3 wt. % absolute error. Following a similar premise, Hillier (2000) obtained the amount of chlorite based on the sum of integrated intensities of both (003) and (004) chlorite reflections. They evaluated their quantitative results from artificially mixed typical clay minerals, and the absolute error was measured as only ±2.2 wt. %.

With the rapid development of computerized methods, many computer programs have been applied in recent years to simplify qualitative and quantitative procedures of the RIR method. Program RUNFIL has been used to compute the relative intensities of measured lines in each phase (Hubbard and Snyder, 1988). Commercial programs MDI Jade and PANalytical X'Pert HighScore feature auto-reflection searching and other calibration conveniences (e.g., auto-measurements of the integrated intensity of a reflection) (Bishop et al., 2011; Nosrati et al., 2012; Wang and Yang, 2013; Zanoni et al., 2016), and NEWMOD software can be used to analyze interstratified clay mineral samples (Reynolds, 1985; Kaminsky et al., 2009; Hooshiar et al., 2012).

In summary, the RIR method is a general instrument-independent constant internal standard method. The RIR method, which is currently one of the most popular internal methods, presents several advantages: i) it is suitable for general use, and the RIR values of one specific clay mineral are sometimes constant and can be used for the quantification of various geological samples (Hubbard and Snyder, 1988) and ii) calibration constants of RIR values can sometimes be calculated from known detailed structural data (Hubbard et al., 1976).

However, the RIR method still presents the following drawbacks: i) most clay minerals do not have specific chemical compositions in geological samples, and thus the parameters of quantitative XRD reflection vary, complicating RIR method use for clay mineral quantification (Brindley, 1980); ii) pure mineral standards are sometimes difficult to obtain;

and iii) effects of clay mineral structural disorder on the quantification reflection intensity are difficult to eliminate.

2.1.2. The MIF method

Every mineral is believed to have a unique mineral intensity factor (MIF value) arising from the unique XRD reflection determined under a given set of experimental conditions. The method that uses a certain internal standard to obtain the MIF value (Table 1) and to further measure the amount of clay minerals is referred to as the MIF method, which was proposed by Moore and Reynolds (1997), and the MIF value is calculated as follows (Środoń et al., 2001):

$$MIF = \left(\frac{I_X}{I_S}\right)\left(\frac{\%S}{\%X}\right) \qquad (6)$$

%X: The mass% of clay mineral X;

%S: The mass% of the standard;

I_X: The intensity of clay mineral X in the XRD pattern of the mixture;

I_S: The intensity of the standard in the XRD pattern of the mixture.

The MIF value does not depend on concentrations of the clay mineral X and standard in mixtures (when a sample is finely ground to eliminate micro-absorption) (Bish and Reynolds, 1989) or on the mass absorption coefficient of a mixture. %X can be obtained from the following formula 7 transformed from formula 6:

$$\%X = \left(\frac{I_X}{I_S}\right)\left(\frac{M_S}{MIF}\right)\left(\frac{100}{M}\right) \qquad (7)$$

where M_S represents the mass of the standard and where M is the total mass of the mineral X and the added standard.

Two key processes are required to be facilitated before the quantification of clay minerals.

Select a suitable internal standard as a primary process. ZnO (Środoń et al., 2001) and pyrophyllite (Moore and Reynolds, 1997; Środoń et al., 2001) have frequently been used as an internal standard. However, ZnO is believed to be better suited as an internal standard of the MIF method. Three advantages of using ZnO as an internal standard are as follows: i) its reflections are at different positions than those of clay minerals and are strong enough to be distinguishable; ii) a small amount (10%) is used; and iii) the particle size of ZnO can be small enough (depending on the supplier) to avoid micro-absorption effects (Snyder and Bish, 1989; Środoń et al., 2001).

Table 1
Some MIF values from Środoń et al. (2001).

Mineral	Reflection d value (nm)	MIF^*_{100}	MIF^*_{002}	MIF^*_{103}
Barite	101 (0.434)	0.12	0.20	0.23
Calcite	104 (0.303)	1.07	1.55	2.05
Plagioclase	002 (0.320)	0.71	1.01	1.32
Pyrite	200 (0.272)	0.94	1.42	1.72
Siderite	018 + 116 (0.172)	0.46	0.66	0.87
2:1 Al clays	060 (0.150−0.151)	0.10	0.14	0.19

The MIF^*_{100} value is obtained from the (100) reflection of ZnO; MIF^*_{002} and MIF^*_{103} values are obtained from the (002) and (103) reflections of ZnO, respectively.

The second step involves obtaining accurate MIF values. The following issues have been raised surrounding XRD reflection information selected for the MIF method with its first application for clay mineral quantification. i) The use of reflections originating from natural clay minerals or of the ideal model for clay minerals simulated by a computer to obtain the MIF value (Moore and Reynolds, 1997): The MIF value obtained by the former was denoted as the measured MIF value and as the latter computer-calculated MIF value. Some researchers have noted that the computer determination approach compared to the former process involves fewer steps and easily prevents man-made errors (Jahanbagloo and Zoltai, 1968; Clark et al., 1973). Some commercial computer programs have thus been applied using the MIF method (Reynolds, 1985). Moore and Reynolds (1997) verified that measured MIF values differ little from computer calculated MIF values, which was subsequently validated by Środoń et al. (2001) (Table 1). ii) The use of the (0l0) reflection or (00l) reflection for clay minerals as the quantification reflection: The (00l) reflection, and especially the (001) reflection, has been used as the quantification reflection in previous studies (Tributh, 1991; Tebbens et al., 1998). However, Kahle et al. (2002) found that some MIF values calculated from the (00l) reflection of clay mineral XRD patterns vary widely, and especially for chlorite (from 0.33 to 1.1), smectite (from 0.22 to 1.0) and vermiculite (from 0.34 to 1.0). This is because (00l)-reflection information for clay minerals is affected by many factors (i.e., chemical compositions, structural defects, and isomorphism). Środoń et al. (2001) advised the use of the (060) reflection to calculate MIF values, as (060) reflection is insensitive to differences in structural and chemical composition. Since then, the (060) reflections of clay minerals have been used as the main quantification reflections in MIF methods (Derkowski et al., 2009; Szczerba and Środoń, 2009; Środoń and Kawiak, 2012; Zeelmaekers et al., 2012). Środoń et al. (2001) also advised the use of side-loading as an XRD sample loading method, which is more suitable for clay mineral samples due to a lack of preferred orientation in clay particles.

Recently, the MIF method has gradually replaced the RIR method in the quantification of clay minerals, as the former saves time and is easy to apply (Kuila and Prasad, 2013; Aburto and Southard, 2016). As the best advantage of the MIF method, once the MIF value of one clay mineral is obtained, the accurate amount of clay minerals is easy to acquire. Moreover, the quantification procedure of the MIF method is uncomplicated and easy to perform.

However, two problems are associated with the MIF method when applied for the quantification of clay minerals: i) inadequate MIF values cannot satisfy the quantification of all clay minerals, although Środoń et al. (2001) have obtained many MIF values and thus applications of the MIF method remain limited and ii) the (060) reflections of some clay minerals such as montmorillonite, kaolinite and illite overlap, making it difficult to identify quantification reflections of each clay mineral during the analysis of natural rock samples.

It is noteworthy that two challenges remain when the RIR and MIF methods are used to quantify clay minerals: i) the quantification of minor clay minerals when their characteristic

quantitative reflections overlap with those of other clay minerals with large amount (Bish and Howard, 1988). This is attributed to the fact that it is very difficult to identify quantitative reflections of clay minerals with little amount; ii) the evaluation of quantitative results. It is still a challenge to assess the content of clay minerals obtained *via* single-reflection methods, although several supplementary methods have been used (e.g., measuring specific surface areas *via* ethylene glycol monomethyl ether (EGME)/H_2O methods or based on cation exchange capacity (CEC) (Środoń and McCarty, 2008).

2.2. Whole pattern methods

As another type of XRD quantification method whereby all intensities of XRD reflections of each mineral sample are obtained by fitting them with parameters from pre-registered pure standard or calibrated crystallographic data is the whole pattern method. Two whole pattern methods are widely used: the Rietveld method and the full pattern summation method. The Rietveld method uses calibrated crystallographic data, and the full pattern summation method uses pre-registered pure standard.

2.2.1. Rietveld methods

The Rietveld method, one of the whole pattern methods, is widely used for clay mineral quantification, and all reflections are simulated by calibrated crystallographic parameters (Rietveld, 1969; Post and Bish, 1989; Lutterotti and Scardi, 1990; Bish and Post, 1993; Scrivener et al., 2004; Haumont et al., 2009). Moreover, detailed structural information on clay minerals can be obtained *via* the Rietveld method, including the positions of exchangeable cations and octahedral and tetrahedral cation ordering (Bish, 1993).

Theoretically, the Rietveld method differs from single reflection techniques in regards to the quantification of clay minerals by XRD analysis in that refinement (a type of gradual fitting) is used for XRD data and is carried out on a point-by-point (step-by-step) basis rather than in relation to individual reflections. The Rietveld refinement minimizes R, which is the sum of weighted and squared differences between observed and calculated intensifies at each point (or 2θ step) in an XRD pattern. The procedure of minimizing R involves least squares refinement (Bish, 1993).

$$R = \sum_i w_i \left| y_i(obs) - y_i(calc) \right|^2 \qquad (8)$$

where y_i(obs) and y_i(calc) are the observed and calculated intensities at point i, w_i is the weight assigned to each intensity, and y_i(calc) is the calculated intensity at each point (or 2θ step), which is determined by summing contributions from the background and all neighboring Bragg reflections as follows:

$$y_i(calc) = S \sum_k (p_k L_k |F_k| G(\Delta\theta_{ik}) P_k) + y_i(bkg) \qquad (9)$$

where S is a phase-specific scale factor, p_k is the multiplicity factor, L_k is the Lorentz and polarization factor for the kth Bragg reflection, F_k is the structure factor for an individual reflection of a particular phase, $G(\Delta\theta_{ik})$ is the reflection profile function, P_k is the preferred orientation function, θ_{ik} is the Bragg angle for the kth reflection, and y_i(bkg) is the refined background. These parameters can be adjusted through a variety of software programs for optimization (for details, see the text below on software programs) to form specific theoretical clay mineral XRD pattern. In multiple clay mineral system, quantitative mineral analysis can be performed by comparing theoretical mineral patterns to practical sample.

The Rietveld method was originally developed to refine powder diffraction data in the analysis of crystalline structures (Rietveld, 1969; Kemper et al., 1972; Sleight et al., 1979; Tanaka et al., 1980). Quantification analysis based on calculated XRD patterns is a natural outgrowth of the Rietveld method in that the refined scale factor (S) for each crystalline phase is related to the amount of the composition present in a sample (Bish, 1993; Ward and French, 2006; Criado et al., 2007; Camilleri, 2008). The Rietveld method has become a powerful tool for quantitative phase analysis with XRD patterns. In 1991, the Rietveld method was first used by Taylor for the quantification of clay minerals (Taylor, 1991; Bish, 1993).

It is noteworthy that most clay minerals have intrinsic characteristics, such as various structures, preferred orientations and chemical compositions, and these characteristics must be taken into account prior to quantitative Rietveld analysis.

Due to the presence of complex structures (e.g., structural defects such as stacking defects), it is difficult to use an ideal structure model for clay minerals to fit actual results. Therefore, various models based on the Rietveld method have been developed for the quantification of clay minerals *via* a Rietveld refinement method (Ufer et al., 2008).

Plançon and Tchoubar (1975) proposed a model for quantifying disordered kaolinite with two types of stacking defects. Based on the model of Plançon and Tchoubar, Drits and Tchoubar (1990) described a model for refining XRD patterns of kaolinites, micas and smectites, and they gave the relationship between different types of layer proportions and probabilities. Artioli et al. (1995) introduced a model for structural defects in kaolinite with four crystallographically different unit layers. The total density of stacking defects in kaolinite was obtained using the model. To make the structure model of clay minerals more suitable for Rietveld quantitative analysis, Viani et al. (2002) proposed a new model for Ca-montmorillonite and a corresponding evaluation method that uses factor R_p. R_p is obtained from formula 10, which indicates final agreement between the observed and calculated patterns.

$$Rp = \frac{\sum |y_i(obs) - y_i(calc)|}{\sum y_i(obs)} \qquad (10)$$

The lower R_p is, the higher the degree of agreement is, and Viani et al. (2002) found that the model is superior to earlier models in terms of montmorillonite quantification according to evaluations of R_p. Ufer et al. (2004) subsequently proposed another model applied in Rietveld method for refining the

XRD patterns of montmorillonite. This model was recently used to quantify hydrothermally altered clay-rich rock samples (Ufer et al., 2015), and disordered characteristics of kaolinite and pyrophyllite were obtained *via* the recursive calculation of structural factors. Moreover, using this model, Reinhard Kleeberg and his colleagues performed well in the Reynolds Cup contest (a round-robin test for quantitative phase analysis) several times (Omotoso et al., 2006), indicating that the model is capable of accurately measuring smectite content.

Moreover, several models (Järvinen, 1993; Kleeberg et al., 2008; Madsen et al., 2012) such as the March model (Dollase, 1986) have been used to eliminate effects of the preferred orientation of clay minerals when side-loading is not used as a preparation method. However, it is noteworthy that inadequate reflections are needed to reliably fit such models, and sometimes a preferred orientation vector and available parameters relating to the degree of preferred orientation should be given.

Some researchers believe that the Rietveld method can be used to determine the chemical compositions of samples (Bish and Howard, 1988; Ban and Okada, 1992). Ban and Okada (1992) proposed the presence of a strong correlation between chemical compositions and the intensity ratio of two characteristic reflections. In this case, the difference in intensity ratios of characteristic reflection may be used to evaluate chemical variability and to avoid the interference of chemical variability for the quantification of clay minerals. As many parameters must be refined and given disturbances incurred on the personal factor during quantitative procedures of the Rietveld method, various software applications for quantitative analysis have been developed to refine the Rietveld method more easily. Such software programs include SIROQUANT (Taylor, 1991) (marketed by SIETRONICS™ Pry Ltd), BGMN (Bergmann et al., 1998), GSAS (General Structure Analysis System) (Larson and Von Dreele, 1994), WYRIET (Schneider and Dinnebier, 1991), BRENDA (Basic Rietveld-ENhanced Diffraction Analysis) (Fuentes-Montero et al., 2007), Highscore (PANalytical™ Company), and TOPAS (TOtal PAttern Solution, Bruker™ Company). Particularly, BGMN, TOPAS and SIROQUANT can yield reliable quantitative phase analysis results (Kaduk, 2009).

2.2.1.1. SIROQUANT.

SIROQUANT was first proposed by Taylor (1978). The prototype of SIROQUANT is a program system that includes four parts (Fig. 1): program PREP (generates (*hkl*)'s multiplicity factor), program STRUCT (generates $F_{(hkl)}$'s structural factor refinement), program ORIENT (produces oriented datasets from unoriented datasets), and TRACSCAL (refines Rietveld parameters).

PREP is applied to generate the multiplicity factors of crystal forms by computing the whole reciprocal lattice of a phase and by grouping reflections of similar 2θ and $F_{(hkl)}$ values (Taylor, 1978). STRUCT calculates structural factors $F_{(hkl)}$ from structural information listed in the Crystal Structure Databank. STRUCT takes (*hkl*) information generated by PREP and produces an (*hkl*) dataset for a phase, listing all (*hkl*), $F_{(hkl)}$, J_k and α_k for use in the main TRACSCAL program. An (*hkl*) dataset is only computed once for a mineral when the orientation plane is changed. The ORIENT program

allows a number of differently oriented (*hkl*) datasets to be produced for TRACSCAL. TRACSCAL is the main program used in the SIROQUANT system. TRACSCAL allows for the multiphase refinement of the following variables to fit a total calculated profile to the measured profile (Taylor, 1991).

As some of the pioneers, Taylor et al. have applied employed the Rietveld method for the quantitative analysis of clay minerals since 1992 (Taylor and Rui, 1992). They proposed an approach employing (*hkl*) files (observed) used through SIROQUANT software in 1994 (Taylor and Matulis, 1994). (*hkl*) files sourced from the measurement of clay minerals rather than from calculated data were used in these refinements for the quantification of clay minerals with imperfectly crystal structures. Taylor and Matulis used measured (*hkl*) files to quantify the mixture of montmorillonite and quartz. Their results show that the observed montmorillonite (*hkl*) file is generally applicable and can be used to quantify montmorillonite in raw samples. Jones et al. (2000) found that observed (*hkl*) files can be universally employed without being restricted to a given instrument.

SIROQUANT has been used by many researchers for the quantification of clay minerals. Hutton and Mandile (1996) used SIROQUANT to calculate the mineral composition of a suite of African and Australian coal samples. They found that the observed (*hkl*) files allowed for inherent atomic disorders and perhaps rarer ones that are not present in available clay mineral standards. To make the quantitative results of SIROQUANT more accurate, Keeling et al. (2000) improved procedures by subtracting the background and recalibrating the intensity for the variable divergence slit. Alves and Omotoso (2009) verified the reliability of observed structure factors $F_{(hkl)}$ of kaolinite, hematite and goethite. The two researchers argue that the observed structure factors $F_{(hkl)}$ are also appropriate for the quantification of other minerals.

2.2.1.2. BGMN.

BGMN is another common Rietveld program used for the quantification of clay minerals (Bergmann et al., 1998). The goal of the BGMN program is the complete elimination of numerical instability and bad convergence. BGMN has a set of unique features that allow for the convenient refinement of multiphase samples including clay minerals. The features are as following (Fig. 2): i) application of numerical background through the use of an advanced peak model and new optimization algorithm; ii) one step calculation of the full parameter set of the starting model; iii) correction of preferred orientations and anisotropic peak broadening; and iv) application of complex disordering models.

Many researchers have established various models of BGMN™ for the quantitative analysis of clay minerals. Ufer et al. (2008) proposed a new structural model for the routine quantitative analysis of smectite samples. The accuracy of the model was verified by X-ray fluorescence data of 36 smectite samples from 16 different locations, showing that their model is appropriate for the quantification of smectite samples. In testing with an artificial mixture, they controlled the absolute error within ±2 wt. %. Ufer et al. (2012) further displayed a recursive algorithm for quantitative analysis of illite-smectite mixed-layer and glauconitic containing samples. They also used the DIFFaX
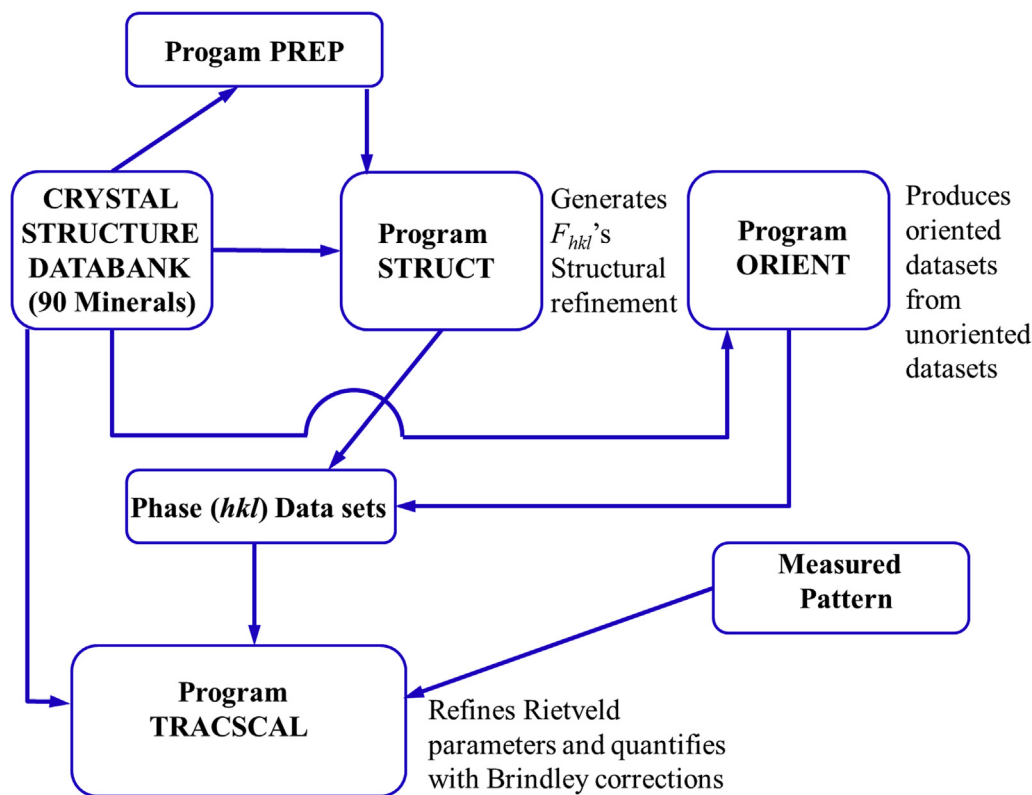
Fig. 1. Flow diagram of the SIROQUANT program system (Taylor, 1991).

as a complementary code to help to simulate non-basal (*hk*) reflections of illites with different degrees of disorder in BGMN. They further used both non-basal and basal reflections to prove that their new approach to clay mineral quantification is reliable. Their results are in good agreement with the actual content of artificially mixed clay samples: absolute errors for illite-smectite mix-layered mineral and smectite were measured as $<\pm1$ wt. %.

BGMN is also suitable for the evaluation of the preferred orientation of clay mineral particles (Kleeberg et al., 2008). Kleeberg et al. (2008) showed that the degree of preferred orientation of particles in XRD samples prepared by different techniques can be evaluated through a correction model implemented in BGMN. They showed that samples prepared by spray-drying are better than those prepared through two other sample preparation methods in terms of reducing preferred orientation (further information can be found in Supporting Information).

2.2.1.3. Other Rietveld software. In addition to SIROQUANT and BGMN, other Rietveld software can now be used for clay mineral quantification.

WYRIET: WYRIET was developed by Schneider and Dinnebier (1991). WYRIET features include the following: control of the diffractometer or densitometer, phase identification and search match (ICDD-file), various smoothing procedures, and least squares XRD reflection refinement. Weidler et al. (1998) analyzed the mineralogical composition of a ferralitic soil collected from southern Mali using the WYRIET software, and the quantitative results were found to be reliable in relation to chemical analysis results.

BRENDA: Fuentes-Montero et al. (2007) developed the Basic Rietveld-ENhanced Diffraction Analysis (BRENDA) software and compared it with other Rietveld software (i.e., Fullprof (Rodriguez-Carvajal, 1990), Rietan (Fujio, 1989), DBWS (Bleicher et al., 2000), and TOPAS (Scarlett et al., 2002)) using basic theoretical parameters (i.e., structure factor) from the Fullprof and PowderCell software. Three samples (a computer-generated mixture sample, a National Institute of Standards and Technology (NIST) reference material sample and a real mineral sample) were tested by BRENDA, and strong reliability was found. As its main advantage, this program is easier to apply than Fullprof (Rodriguez-Carvajal, 1990).

GSAS: The general structure analysis system (GSAS) software was first developed by Larson and Von Dreele (1994), is accessed through the EXPGUI interface and was further developed by Toby (2001). Gualtieri et al. (2010) investigated Italian clay samples by Rietveld refinement through GSAS. Gualtieri et al. also combined the internal standard method with the Rietveld technique to quantitatively determine glass content. Their results were verified as reliable through an XRF test. GSAS is designed to be easy to use, and it features a menu driven editor (EXPEDT) equipped with helpful listings and error trapping features. EXPEDT is used to prepare all inputs for GSAS calculation programs. The entire GSAS system is written in the FORTRAN language and uses system callable features.

TOPAS: Scarlett et al. (2002) used the TOPAS program Bruker™ AXS and developed a procedure for the calibration of partial or unknown structures *via* the Rietveld method.
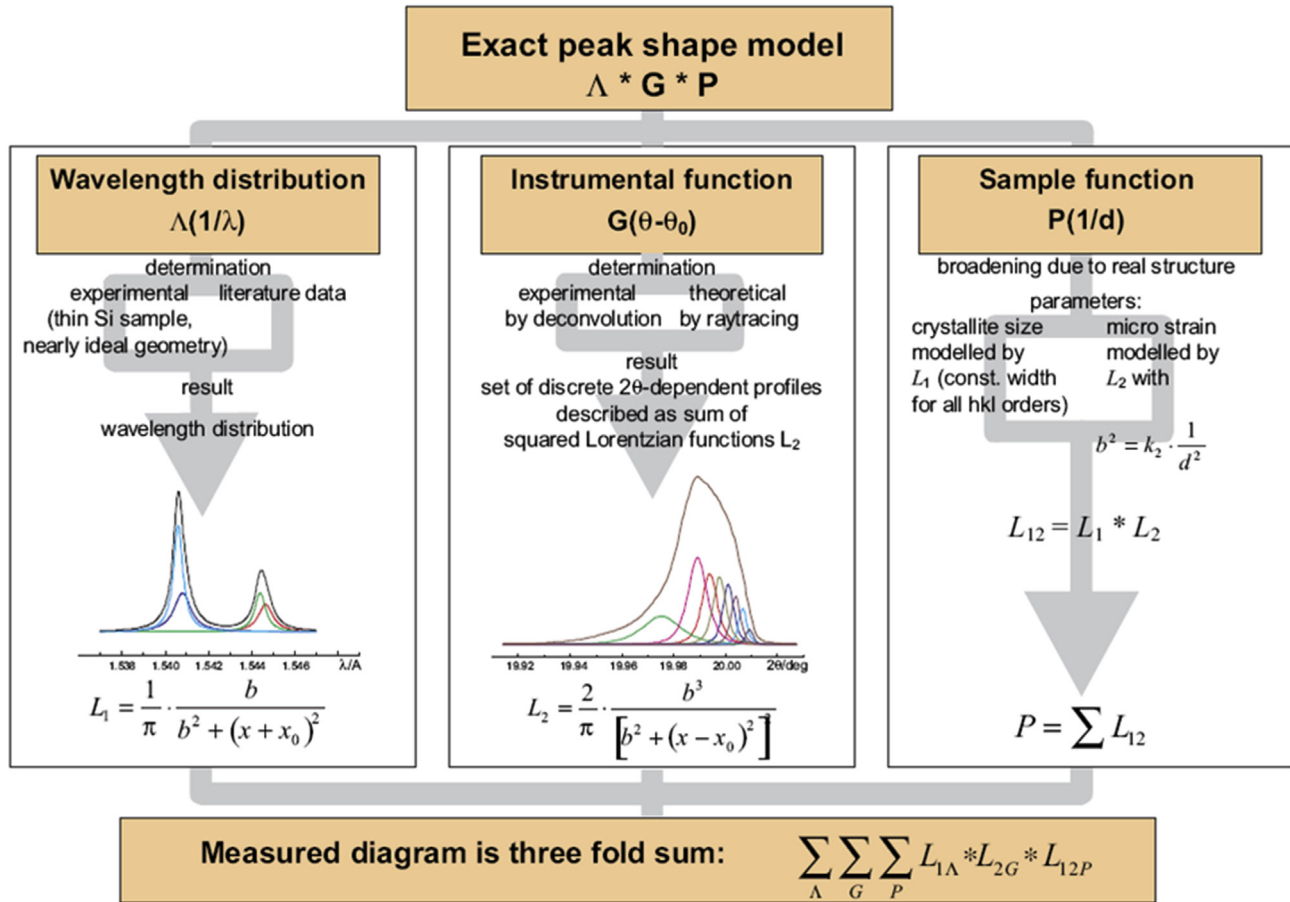
Fig. 2. XRD pattern model used in the BGMN program (Bergmann et al., 1998; Taut et al., 1998). L_1, L_2 and L_{12} are the Lorentzian functions where d is the d-spacing. All calculations of the peak shape models are carried out at the $1/\lambda$ and $1/d$ scales, respectively; x and x_0 are used for scale positions in reciprocal space; b refers to any peak breadth (Lorentzian functions) on the $1/d$ scale; k_2 is the square of the usual microstrain.

Phases that have not been identified or fully characterized may be easily quantified as a group along with any amorphous material in a sample. Certain parameters that can be refined and that affect reflection positions, shapes, and relative intensities may also be applied in TOPAS. As its main features, TOPAS offers (i) a computer algebra system for function minimization and for the application of linear/non-linear constraints; (ii) a fully functional Rietveld program for laboratory X-ray diffraction, synchrotron, single-crystal and neutron fixed wavelength data; and (iii) a simulated annealing algorithm for all systems including structure solution in real space from powder, neutron and single-crystal data.

Among these programs, SIROQUANT is not the most sophisticated, but it is designed specifically for quantitative phase analysis with a user friendly interface and a database of >300 phase entries. The refinement strategy employed is relatively simple (Hillier, 2000).

Totally, the Rietveld method is suitable for treating the overlapped reflections of XRD patterns than the single reflection method (Santini, 2015). Moreover, the Rietveld method is of a highly programmed and automated nature and thus more suitable for some special field work (Deng et al., 2015) (e.g., as an XRD analysis instrument of the Curiosity Rover for Mars exploration (Blake et al., 2012)). Other advantages of Rietveld method include the following: i) the degree of preferred orientation of clay minerals can be evaluated and ii) to some extent, the Rietveld method can be used to evaluate the approximate chemical compositions of clay minerals. However, when using the Rietveld method, long periods of time is typically required for data collection (Hillier, 2000).

2.2.2. Full pattern summation method

The full-pattern summation method, an important whole pattern method, is based on the principal that the observed diffraction pattern is the sum of individual phases that compose a sample (Smith et al., 1987; Batchelder and Cressey, 1998; Chipera and Bish, 2002, 2013). Full pattern summation methods have been applied *via* the use of clay mineral quantitative methods in recent decades.

When employing the full pattern summation method, X-ray data are first entered into the full pattern summation program. Then, parameters of standard clay minerals are selected. The program automatically fits the sum of stored XRD patterns (the calculated patterns) of pure standard clay minerals to measured patterns by varying the fraction of each mineral standard pattern. The Solver function in Microsoft Excel is often used to minimize a degree of fit parameters between

calculated and measured patterns. The calculation analyzes the pattern to find XRD reflection intensities for clay minerals. XRD reflection intensities for each clay mineral then are determined from proportions of each clay mineral standard pattern required to ensure the best fit. These reflection intensities then are compared to the reflection intensity of the internal standard, and the weight percentages of clay minerals are obtained by calculating from measured mineral intensity ratios (Eberl, 2003, 2004).

RockJock and FULLPAT are the two main software of full pattern summation for the quantification of clay minerals and are introduced as follows (Eberl, 2003; Chipera and Bish, 2013). For example, Eberl (2003) evaluated the accuracy of the RockJock program by using artificially mixed clay samples, and found only 1 or 2 wt. % absolute error. Christidis et al. (2006) applied RockJock to determine the smectite content of 24 smectite samples. They further compared RockJock results to those of other complementary tests and found RockJock to yield reliable results. Cheshire et al. (2013) used FULLPAT to determine smectite content to study smectite evolution at elevated pressures and temperatures. Vaniman et al. (2014) used FULLPAT to analyze long-range data collected from the Mars Science Laboratory rover *Curiosity*. They found that clay minerals comprised approximately 20% of the mudstone samples from the study area.

RockJock employs similar procedures as FULLPAT. They differ in that RockJock is more automatized. It is possible to evaluate fit reliabilities *via* full pattern summation procedures, and it is also more efficient when applied for full pattern summation relative to Rietveld methods. Unlike the Rietveld method, the full pattern summation method does not require the use of crystal structure files (Mertens et al., 2006). However, the accuracy of full pattern summation quantification is affected by the data quality of standard patterns available through software like RockJock.

As noted above, single reflection and whole pattern methods are the most widely applied quantitative XRD methods as shown by results of the largest quantitative clay mineral analysis competition, the Reynolds Cup, a global competition about the clay mineral quantification (McCarty, 2002; Raven, 2015).

For example, in the latest two contests (the 7th and 8th Reynolds Cup contests), the Rietveld method was most widely used method. The first-place teams of 7th and 8th contests used this type of method. Full pattern summation methods were also used by many participants. The second-place team of the 7th contest and the third-place team of the 8th contest applied full pattern summation methods. In total, 15% and 17% of the participants used single reflection methods (RIR and MIF methods) for the 7th and 8th contests, respectively. These methods are the most widely used by participants of Reynolds Cup competitions. Among them, Rietveld and full pattern summation methods have been applied more widely than single reflection methods in Reynolds Cup contests, but it is noteworthy that single reflection methods are also precise when applied to certain clay minerals as shown by low clay mineral bias results of the 7th contest (Plötze, 2014; Kleeberg, 2016).

As noted above, from the results of Reynolds Cup contests, challenges of clay mineral quantification still relate to the existence of variable chemical compositions, variable structures and preferred orientation. For example, the absolute errors of montmorillonite and saponite were still pronounced, and analysis accuracies of different degree of defect of kaolinite and halloysite are not sufficient.

3. Conclusions

It must be noted that the abovementioned quantification methods involve the use of assistant techniques such as FTIR and elemental analysis (Jordá et al., 2015) for mineral identification and for selecting the right quantification standards. In this case, supplementary methods are favorable for the quantification of clay minerals.

In conclusion, the quantification of clay minerals is still a challenge and possibly involves large analytical errors due to various chemical compositions and structures and preferred orientation effects. Although many quantification methods based on the XRD technique are believed to be highly accurate, analysis results mostly depend on human factors. Moreover, sample preparation, data processing and the selection of standards are essential for the XRD quantification of clay minerals.

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.sesci.2017.12.002.

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