

## OUTCOMES OF 12 YEARS OF THE REYNOLDS CUP QUANTITATIVE MINERAL ANALYSIS ROUND ROBIN

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**Abstract**—In 2000, The Clay Minerals Society established a biennial quantitative mineralogy round robin. The so-called Reynolds Cup competition is named after Bob Reynolds for his pioneering work in quantitative clay mineralogy and exceptional contributions to clay science. The first contest was run in 2002 with 40 sets of three samples, which were prepared from mixtures of purified, natural, and synthetic minerals that are commonly found in clay-bearing rocks and soils and represent realistic mineral assemblages. The rules of the competition allow any method or combination of methods to be used in the quantitative analysis of the mineral assemblages. Throughout the competition, X-ray diffraction has been the method of choice for quantifying the mineralogy of the sample mixtures with a multitude of other techniques used to assist with phase identification and quantification. In the first twelve years of the Reynolds Cup competition (2002 to 2014), around 14,000 analyses from 448 participants have been carried out on a total of 21 samples. The data provided by these analyses constitute an extensive database on the accuracy of quantitative mineral analyses and also has given enough time for the progression of improvements in such analyses. In the Reynolds Cup competition, the accuracy of a particular quantification is judged by calculating a “bias” for each phase in an assemblage. Determining exactly the true amount of a phase in the assemblage would give a bias of zero. Generally, the higher placed participants correctly identified all or most of the mineral phases present. Conversely, the worst performers failed to identify or misidentified phases. Several contestants reported a long list of minor exotic phases, which were likely reported by automated search/match programs and were mineralogically implausible. Not surprisingly, clay minerals were among the greatest sources of error reported. This article reports on the first 12 years of the Reynolds Cup competition results and analyzes the competition data to determine the overall accuracy of the mineral assemblage quantities reported by the participants. The data from the competition were also used to ascertain trends in quantification accuracy over a 12 year period and to highlight sources of error in quantitative analyses.

**Key Words**—Accuracy, Clay Minerals, Mineralogy, Quantitative Analysis, Reynolds Cup, Round Robin, X-ray Diffraction.

### INTRODUCTION

Quantitative phase analysis has made considerable advancements in the last 20 to 30 years due not in the least to rapid developments in computer hardware and software. Concurrently, advances in analytical instrumentation and techniques have also been developed to provide analysts with a multitude of techniques to apply to quantitative phase analysis. With ready access to high-speed computers, better software, higher instrument sensitivity, and new instrument techniques, quantitative phase analysis is available to any well-equipped laboratory and is, therefore, being applied to increasingly complex mineral assemblages. Clay minerals represent some of the most complex natural materials and clay minerals are used in a vast number of industrial applications (Harvey and Lagaly, 2013), including common uses in petroleum exploration and extraction, mineral exploration, mining and processing, building

and construction materials, industrial minerals (e.g. paper, plastic, and rubber), food, and cosmetics. Increasingly, commercial, academic, and government laboratories are being asked to provide quantitative phase analysis on a wide range of materials and compositions with little or no “standards” or “reference” materials to validate their results. With this in mind, several groups have devised round robins to test precision and accuracy using natural and synthetic mineral mixtures. Madsen *et al.* (2001) described the first part of a quantitative phase analysis round robin sponsored by the International Union of Crystallography (IUCr) Commission on Powder Diffraction (CPD) using eight samples of relatively simple three-phase mixtures of well-ordered corundum, fluorite, and zincite. While mixtures with the compositions used in that round robin were unlikely to be found together in nature, the mixtures were used to test the precision and accuracy that could be expected from powder X-ray diffraction (XRD) under ideal conditions. Scarlett *et al.* (2002) reported the results of the other samples of the IUCr CPD round robin that targeted specific problems in quantitative phase analysis. These problems included

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preferred orientation, amorphous material content, and micro-absorption. The samples used in the Scarlett *et al.* (2002) study were a synthetic bauxite mineral mixture, a natural rock of unknown composition (granodiorite), and pharmaceuticals with and without amorphous material.

Ottner *et al.* (2000) organized a round robin in which sample splits from two naturally occurring clay-rich samples of unknown composition were distributed to 19 external laboratories for quantitative analysis. Results of the round robin identified poor qualitative analysis as the primary source of errors, but pre-treatment methods, sample preparation, and quantitative analysis also contributed to errors. Calvert *et al.* (1989) were the first to report the outcomes of a “blind test” on four samples that contained mixtures of purified minerals prepared to represent “rock-like” compositions (two sandstones, one shale, and one limestone). The tests were used to gauge the accuracy of five commercial laboratories for quantitative mineralogy. A subsequent round robin that was also based on the use of mixtures of relatively pure-phase minerals with specific emphasis on clay minerals was made by Środoń *et al.* (2001). Three samples of synthetic mixtures with compositions that are typically present in natural shale materials were sent to a limited number of external laboratories for analysis. In light of the problems that were identified by previous round robins for quantitative phase analysis of materials that contain clay minerals, Douglas McCarty, Jan Środoń, and Dennis Eberl established a round robin in 2000 called the “Reynolds Cup” with some seed funding from The Clay Minerals Society, Chevron USA Inc., and the United States Geological Survey (USGS) (McCarty, 2002). The first round robin was run in 2002, was devised as a biennial event, and was named in honor of Robert C. Reynolds, Jr.’s exceptional contributions to clay science and quantitative phase analysis. The Reynolds Cup is held in a competitive spirit with the added incentive that the top three entrants receive an engraved plaque. The winner is presented with the prestigious Reynolds Cup (Figure 1) perpetual trophy and the honor of being the world’s top quantitative mineral analyst. The contest utilizes three synthetic sample mixtures made from purified natural or synthetic mineral phases that represent realistic sedimentary and weathered rock compositions. The round robin is open to anyone interested in quantitative mineralogy using any technique available to the participant. Each biennial contest is announced either late in odd-numbered years or early in even-numbered years. The registration of sample sets for the competition are also invited. The sample sets are mailed to registered participants with a deadline of approximately 3 months for the return of results. The deadline is specified so that results can be collated and winners notified with sufficient time to attend the annual conference of The Clay Minerals Society. In 2014, the 12<sup>th</sup> year and 7<sup>th</sup> Reynolds Cup quantitative mineralogy competition was held and a total

of 81 sets of three samples were distributed to participants in 21 countries. Samples are made available to individuals in commercial, industrial, government, and academic laboratories. Participants who return results are judged on a simple sum of biases between the submitted percentages and the actual weight percentages ( $W$ ) of all three samples using the equation:

$$\text{Total bias} = \sum_{j=1}^3 \sum_{i=1}^{n_j} \text{Abs}[W_{ij}(\text{submitted}) - W_{ij}(\text{actual})]$$

where  $j$  represents each sample,  $i$  represents each phase in the sample (including misidentified phases where  $W_{ij}[\text{actual}] = 0$ ), and  $n_j$  is the total number of phases in the sample plus the number of misidentified phases. The participant with the lowest bias is deemed the winner of the Reynolds Cup competition (McCarty, 2002; Kleeberg, 2005; Omatoso *et al.*, 2006). The winner of the Reynolds Cup is invited to chair the Reynolds Cup organizing committee and to prepare the sample mixtures for the next round robin competition to be held two years later.



Figure 1. The Reynolds Cup Trophy.

Table 1. Non-clay minerals used in the Reynolds Cup samples. The values in parentheses indicate the number of times that the mineral was used in the 21 samples.

|                  |                |                   |
|------------------|----------------|-------------------|
| Quartz (21)      | Anhydrite (3)  | Zircon (3)        |
| Cristobalite (1) | Celestine (1)  | Spinel (1)        |
| K-feldspar (16)  | Barite (5)     | Opal-CT (1)       |
| Plagioclase (17) | Alunite (1)    | Amphibole (4)     |
| Calcite (14)     | Hematite (8)   | Zeolite (2)       |
| Dolomite (11)    | Goethite (6)   | Epidote (1)       |
| Magnesite (5)    | Magnetite (5)  | Birnessite (1)    |
| Aragonite (3)    | Anatase (11)   | Arcanite (1)      |
| Huntite (1)      | Rutile (5)     | Amorphous (8)     |
| Nahcolite (1)    | Ilmenite (3)   | Silica            |
| Halite (6)       | Gibbsite (4)   | Volcanic glass    |
| Pyrite (7)       | Böhmite (2)    | Opaline silica    |
| Siderite (8)     | Fluorite (2)   | $\gamma$ -alumina |
| Gypsum (4)       | Apatite (2)    | Allophane         |
| Bassanite (1)    | Tourmaline (4) | Ferrihydrite      |

## METHODS

### *Reynolds Cup Samples*

In the 12 years since the inception of the Reynolds Cup, 21 individual samples containing a combined total of 39 non-clay (Table 1) and eight clay mineral groups (Table 2) have been sent to 448 participants or group of participants. The following list of fourteen synthetic rock types indicates the variety that has been represented over the course of the first seven Reynolds Cup contests: mudstone, sandstone, siltstone, calcareous mudstone, saline sedimentary rock, sediment from an evaporite environment, a sample to represent a hydrothermal alteration environment, soil formed in a parent material rich in ferromagnesian minerals and amorphous soil minerals, petroleum shale, nickel laterite, bauxite, gypsiferous Keuper, activated bentonite, and kaolin clay. Quartz was the most common non-clay mineral in the competition samples and was present in all 21 samples. In the 21 samples, quartz concentrations ranged from 2 to 46 wt.%. Feldspar minerals, both potassium

and plagioclase forms, were the second most common non-clay minerals in the samples followed by carbonates, iron and titanium oxides, halite, pyrite, amorphous phases, sulfates, and several other minor mineral phases. Dioctahedral 2:1 clay minerals with concentrations between 6 and 48 wt.% were the most common clay minerals, while kaolin group minerals (kaolinite and halloysite) were the second most common clay mineral group in the samples. Minerals of the chlorite group (clinochlore and ripidolite) were commonly included in the samples. A third of all 21 of the Reynolds Cup samples contained 2:1 trioctahedral clay minerals. Other minor clay minerals in the samples included talc, serpentine (lizardite), sepiolite, and palygorskite.

### *Sample Preparation*

Organizers of the first Reynolds Cup in 2002 prepared enough bulk material for approximately 40 sets of three artificial clay-bearing sample sets (~4 g each sample). Because the popularity of the contest has

Table 2. Clay minerals used in the Reynolds Cup samples. The values in parentheses indicate the number of times that the mineral was used in the 21 samples.

|  |   |
|--|---|
| 2:1 Dioctahedral Clay Minerals (21)                                  | Kaolin Group (17)                       |
| Smectite (montmorillonite, nontronite)                               | Kaolinite (well and poorly-ordered)     |
| Interstratified clay minerals (illite-smectite, glauconite-smectite) | Halloysite                              |
| Mica/illite (muscovite $2M_1$ , illite $1M_d$ , $1M$ )               | Dickite                                 |
| 2:1 Trioctahedral Clay Minerals (7)                                  | Other Clay Minerals (21)                |
| Smectite (saponite)  | Chlorite (14 - clinochlore, ripidolite) |
| Vermiculite  | Serpentine (2 - lizardite)              |
| Interstratified clay minerals (corrensite)                           | Talc (3)                                |
| Mica (biotite)   | Sepiolite (1)                           |
|  | Palygorskite (1)                        |

increased, the number of sample sets was increased to 81 sets for the 2014 round robin. Mineral specimens were obtained from private collections, commercial sources, museum mineral collections, and the Clay Minerals Society (CMS) Source Clays Repository (<http://www.clay.org/SOURCE%20CLAYS/SCavailable.html>). Most natural mineral specimens are rarely available in sufficient quantities in the pure form. In order to obtain enough material to prepare approximately 320 g of each sample mixture, some form of purification was required, with the method of purification dependent on the nature of the mineral. Hand picking is sufficient for large mono-mineral grains where color and/or shape can be used to separate the phases. Sieving is effective if the mineral phases show bimodal particle size distributions. Magnetic separation, either by the use of a hand magnet or a Franz magnetic separator, can be used either to obtain a purified magnetic fraction or to remove magnetic materials from a targeted non-magnetic phase. Purification by the use of chemical treatments is effective in removing unwanted phases. For example, acid treatments can be used to remove carbonates from acid-insoluble mineral phases. Clay minerals are readily separated from most non-clay minerals by sedimentation or centrifugation. Several size fractions can be extracted, which depends on what type of clay mineral is purified. Kaolin, chlorite, and illite are usually found in the coarser, <2  $\mu\text{m}$  fraction, whereas clay minerals of the smectite group are usually extracted from the fine clay fraction (*i.e.* <0.2  $\mu\text{m}$ ). When all else fails and sufficient natural specimens cannot be obtained by purification, then high-purity minerals can be obtained by synthesis. For example,

barite can be prepared by adding excess  $\text{Na}_2\text{SO}_4$  to a  $\text{BaCl}_2$  solution and the barite can be recovered by centrifugation and washing. Iron (oxyhydr)oxides can be prepared by the methods given by Schwertmann and Cornell (2000). The preparation of purified standard mixtures requires that the particle size be approximately the same for each phase so that the phases can be mixed relatively easily. For the 2012 Reynolds Cup competition (Raven and Self, 2012), this was achieved by hand grinding the individual dry standards and using a sieve to separate the <400  $\mu\text{m}$  fraction for the major phases and the <200  $\mu\text{m}$  or <100  $\mu\text{m}$  fractions for the minor and trace phases. After sieving, the mineral phases were checked for purity using X-ray diffraction (XRD) and were allowed to equilibrate at room temperature (22°C) and humidity (20%) for several days prior to weighing. Equilibration at room temperature and humidity is particularly important for moisture sensitive phases, such as smectites and interstratified clay minerals. The samples were mixed using a ball mill that contained only a few large balls, which was sufficient to break up agglomerated particles. Milling was followed by end over end shaking in a large plastic or glass container. Up to five grab samples were taken from each mixture and tested for homogeneity using XRD (Figure 2) and X-ray fluorescence (XRF) analyses (Table 3). The XRD samples were prepared by grinding approximately 1.5 g of each of the six mixtures in 10 mL of ethanol for 10 min using agate grinding pieces in a McCrone micronizing mill. The sample slurries were oven dried at 60°C and then thoroughly mixed in an agate mortar and pestle before the samples were lightly back pressed into stainless steel sample holders for XRD measurement.

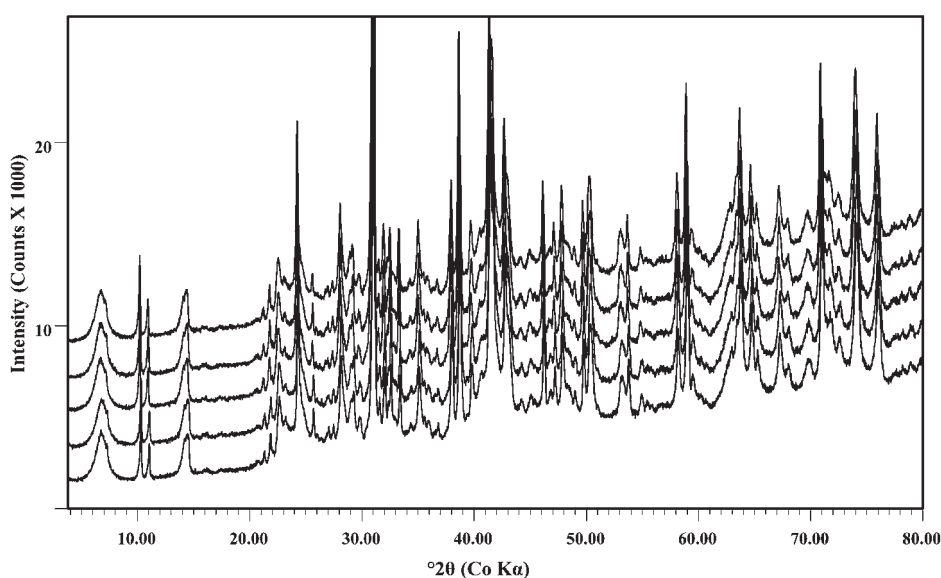


Figure 2. XRD random powder patterns of five grab samples of the 2012 Reynolds Cup Sample number two, which was used for a test of homogeneity. Samples were micronized for 10 min in ethanol, oven dried at 60°C, lightly back pressed into sample holders, and analyzed using a PANalytical X'Pert Pro MPD with variable divergence slits and silicon strip detector.

Table 3. Homogeneity check of five grab samples of Sample 2 from the 2012 Reynolds Cup using XRF analysis (wt.%) that show the maximum, minimum, mean, standard deviation, and coefficient of variation of the five measurements with the results reported on a 105°C dried basis.

|                                | 2A    | 2B    | 2C    | 2D    | 2E    | Mean  | Stdev | CoV   | max   | min   |
|--------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| SiO <sub>2</sub>               | 43.81 | 44.16 | 43.72 | 44.10 | 43.97 | 43.95 | 0.19  | 0.004 | 44.16 | 43.72 |
| TiO <sub>2</sub>               | 0.34  | 0.34  | 0.33  | 0.34  | 0.34  | 0.34  | 0.00  | 0.007 | 0.34  | 0.33  |
| Al <sub>2</sub> O <sub>3</sub> | 8.68  | 8.67  | 8.64  | 8.64  | 8.63  | 8.65  | 0.02  | 0.002 | 8.68  | 8.63  |
| Fe <sub>2</sub> O <sub>3</sub> | 26.48 | 26.19 | 26.53 | 26.42 | 26.43 | 26.41 | 0.13  | 0.005 | 26.53 | 26.19 |
| MnO                            | 0.06  | 0.06  | 0.06  | 0.06  | 0.06  | 0.06  | 0.00  | 0.006 | 0.06  | 0.06  |
| MgO                            | 10.92 | 10.91 | 10.86 | 10.81 | 10.83 | 10.87 | 0.05  | 0.004 | 10.92 | 10.81 |
| CaO                            | 0.46  | 0.46  | 0.45  | 0.46  | 0.46  | 0.46  | 0.00  | 0.005 | 0.46  | 0.45  |
| Na <sub>2</sub> O              | 0.69  | 0.70  | 0.70  | 0.70  | 0.70  | 0.70  | 0.00  | 0.006 | 0.70  | 0.69  |
| K <sub>2</sub> O               | 1.55  | 1.58  | 1.56  | 1.59  | 1.57  | 1.57  | 0.01  | 0.009 | 1.59  | 1.55  |
| P <sub>2</sub> O <sub>5</sub>  | 0.04  | 0.04  | 0.04  | 0.04  | 0.04  | 0.04  | 0.00  | 0.012 | 0.04  | 0.04  |
| SO <sub>3</sub>                | 0.01  | 0.01  | 0.01  | 0.01  | 0.01  | 0.01  | 0.00  | 0.077 | 0.01  | 0.01  |
| Cl                             | 0.01  | 0.01  | 0.01  | 0.01  | 0.01  | 0.01  | 0.00  | 0.073 | 0.01  | 0.01  |
| Sum                            | 93.05 | 93.13 | 92.92 | 93.18 | 93.04 | 93.06 | 0.10  | 0.001 | 93.18 | 92.92 |

The XRD data were collected on a PANalytical (PANalytical B.V., Almelo, The Netherlands) X'Pert Pro Multi-purpose diffractometer using a broad focus Co X-ray tube at 45 kV and 55 mA in Bragg-Brentano mode using theta-theta goniometer geometry. Radiation from the incident Fe-filtered X-ray beam was kept entirely within the sample area throughout the angle scan range by using a 20 mm mask, an automatic theta-compensating divergence slit set to 8.5 mm, and 2° fixed anti-scatter slits. The goniometer scan range was between 4 and 80 °2θ with a 0.016 °2θ step size. The XRD patterns were collected using a PANalytical X'Celerator 1D silicon-strip, 128 element detector in scanning mode for a total data collection time per sample of approximately 30 min. The XRF samples were prepared by accurately weighing approximately 1 g of each oven dried (105°C) sample mixture and mixing with 4 g of 12–22 Li tetraborate/metaborate flux. The mixtures were heated to 1050°C in a Pt/Au crucible for 20 min to completely dissolve the sample and were then poured into a 32 mm Pt/Au mold heated to a similar temperature. The melt was cooled rapidly over a compressed-air stream and the resulting glass disks were analyzed on a 4 kW PANalytical Axios Advanced wavelength-dispersive XRF system equipped with a Rh end-window X-ray tube. Any sample mixtures that showed significant inhomogeneity were passed through a 400 μm sieve, re-mixed using the procedure given above, and re-tested for homogeneity before proceeding. The XRD (Figure 2) and XRF (Table 3) analysis data showed that the samples were very well homogenized.

Organizers of the other Reynolds Cup contests used a number of different strategies to prepare homogeneous mixtures. These included a TURBULA® shaker-mixer (Glen Mills Inc., 220 Delawanna Ave, Clifton, New Jersey 07014, USA <http://www.glenmills.com/powder-blending/turbula-shaker-mixer/>) that was used in the 2008 contest and an Inversina® tumbler mixer

(Bioengineering AG, Wald, Switzerland <http://www.inversina.com/main/inversina21>) that was used in the 2014 contest. Several methods of splitting the samples were employed for each of the round robins: random sampling, louver splitter, cone splitter, and rotary splitter. For all competitions, the bulk mixtures were split into approximately 4 to 5 g aliquots, which from 2002 to 2012 resulted in between 40 and 120 sample sets for distribution to participants. Sample sets were packaged and sent *via* mail to the registered participants' addresses and the participants were given between 2 and 4 months to complete the analyses and return the results (the time allowed depended on the annual CMS meeting). Participants were encouraged to either return their results or the unopened packages before the deadline in order to be eligible to enter subsequent Reynolds Cup contests.

#### Participants

A summary of the six Reynolds Cup contests held between 2002 and 2014 (Table 4) showed a steady increase in the number of participants, but more significantly, the percentage of participants who returned results more than doubled since the first contest in 2002. In 2014, there were 81 registrants from 21 countries, which confirmed the international significance of the round robin (Table 5). The USA contributed the most registrants, followed by Germany with the second most, and by Australia and Russia with the third most registrants.

#### Analytical techniques

Over 96% of participants used XRD as their primary technique for qualitative and quantitative analysis and less than 4% used other techniques, such as Fourier-transform infrared (FTIR) spectroscopy, Raman spectroscopy, scanning/transmission electron microscopy, and Mössbauer spectroscopy. A large number of ancillary

Table 4. Summary of the seven Reynolds Cup round robins between 2002 and 2014.

| Year         | Participants | Results returned | Percentage returned | Number of mineral phases |
|--------------|--------------|------------------|---------------------|--------------------------|
| 2002         | 40           | 15               | 37.5                | 36                       |
| 2004         | 60           | 34               | 56.7                | 34                       |
| 2006         | 64           | 37               | 57.8                | 42                       |
| 2008         | 53           | 42               | 79.2                | 35                       |
| 2010         | 76           | 63               | 82.9                | 42                       |
| 2012         | 74           | 62               | 83.8                | 40                       |
| 2014         | 81           | 67               | 82.7                | 61                       |
| Total (mean) | 448 (64.0)   | 320 (45.7)       | (68.6)              | 290 (41.4)               |

techniques, however, were used by participants to aid with phase identification and quantification and included: XRF, inductively coupled plasma atomic emission spectroscopy (ICP-AES), inductively coupled plasma optical emission spectroscopy (ICP-OES), neutron activation, FTIR, visible and near-infrared (VNIR) reflectance, differential thermal analysis (DTA), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), scanning electron microscopy (SEM), transmission electron microscopy (TEM) with energy dispersive X-ray spectroscopy (EDX), wet chemistry, cation exchange capacity (CEC), LECO<sup>®</sup> furnace elemental analysis, surface area, optical microscopy/petrology, Mössbauer spectroscopy, and ion chromatography. Of the more than 96% of participants that used XRD as their primary analysis technique, most also employed a number of sample preparation procedures to aid their analysis. Results obtained from bulk pressed powders were ultimately used in their final submissions, but were assisted by using a variety of separation techniques, such as magnetic fractionation, optical separation, grain size separation by wet or dry sieving, and fine particle separation using dispersion and sedimentation (either by gravity or centrifuge). Clay or fine-clay fractions were usually prepared as oriented

Table 5. Country of origin of the participants of the 2014 Reynolds Cup. Number of registered participants or participant groups from each country and the number of registrants who returned results are shown in parentheses.

|                   |                                  |
|-------------------|----------------------------------|
| Australia (6/4)   | Poland (3/3)                     |
| Austria (2/1)     | Russia (6/4)                     |
| Belgium (2/2)     | Saudi Arabia (2/0)               |
| China (1/1)       | Slovakia (1/1)                   |
| Colombia (3/3)    | Spain (3/1)                      |
| France (5/5)      | Switzerland (2/2)                |
| Germany (13/12)   | Turkey (2/2)                     |
| Greece (1/1)      | United Kingdom (4/4)             |
| Hungary (1/1)     | United States of America (21/18) |
| Italy (1/1)       | Uruguay (1/0)                    |
| South Korea (1/1) |                                  |

specimens and then subjected to cation exchange, organic liquid solvation (ethylene glycol, glycerol, and formamide), and heating to various temperatures. Several XRD methods were used for quantitative analysis which included single peak (19.4% of participants), whole pattern (19.1%), and Rietveld (57.4%) analysis techniques. The matrix-flushing technique of Chung (1974) along with the reference intensity ratio method (Hubbard and Snyder, 1988) were the methods of choice for those using single peak methods. Whole pattern techniques that were used included Arquant (Blanc *et al.*, 2007), FULLPAT (Chipera and Bish, 2002), X-LS Mineral (Hillier, 2003), QUANTA (Mystkowski *et al.*, 2002), GIFF (Rancort and Dang, 2005), and RockJock (Eberl, 2003). Rietveld methods were the most popular of the XRD quantification techniques with participants using a range of different programs to do the analysis, which included Autoquan/BGMN (Bergmann and Kleeberg, 1998), Fullprof (Rodriguez-Carvajal and Roisnel, 1998), GSAS (Larson and Von Dreele, 2000), HighScore Plus (PANalytical B.V., Almelo, The Netherlands), MAUD (Lutterotti *et al.*, 1999), Quanto (Altomare *et al.*, 2001), RIQAS (Materials Data, Incorporated, Livermore, California), SIROQUANT (Sietronics Pty Ltd, Mitchell, ACT), and TOPAS (Bruker AXS GmbH, Karlsruhe, Germany). Clay minerals and in particular interstratified clay minerals were often characterized by matching the XRD patterns of oriented clay fractions with theoretical patterns generated by computer programs specifically designed for the XRD analysis of clay minerals. The commonly used programs for this purpose were NEWMOD (Reynolds, 1983) and Sybilla (Aplin *et al.*, 2006).

## RESULTS

Results submitted to the Reynolds Cup organizers were copied into separate worksheets of an Excel spreadsheet (Table 6) with any information that served to identify the participant removed in order to maintain confidentiality. At the completion of the contest and approximately 2 weeks before the annual CMS meeting,

Table 6. Example of the results in a spreadsheet that shows the mineral name, actual weight percent, submitted weight percent, and bias for the sample set distributed to participants. These results are for the winner of the 2004 Reynolds Cup.

| Mineral                       | RC2-1  |             |          | RC2-2  |             |          | RC2-3  |             |          |
|-------------------------------|--------|-------------|----------|--------|-------------|----------|--------|-------------|----------|
|                               | (wt.%) | Adj. (wt.%) | $\Delta$ | (wt.%) | Adj. (wt.%) | $\Delta$ | (wt.%) | Adj. (wt.%) | $\Delta$ |
| Quartz                        | 24.8   | 25.1        | 0.3      | 45.7   | 47.0        | 1.3      | 14.7   | 14.8        | 0.1      |
| K-Feldspar                    | 8.5    | 8.3         | 0.2      | 9.2    | 9.5         | 0.3      | 2.1    | 2.9         | 0.8      |
| Albite                        | 6.5    | 8.3         |          | 4.0    | 11.7        |          | 0.0    | 3.7         |          |
| Oligoclase                    | 0.0    |             |          | 6.7    |             |          | 2.9    |             |          |
| Plagioclase                   | 6.5    | 8.3         | 1.8      | 10.7   | 11.7        | 1.0      | 2.9    | 3.7         | 0.8      |
| Calcite                       | 5.0    | 5.3         | 0.3      | 0.0    |             |          | 18.6   | 17.7        | 0.9      |
| Dolomite                      | 2.0    | 2.1         | 0.1      | 0.0    |             |          | 6.0    | 5.8         | 0.2      |
| Magnesite                     | 0.0    |             |          | 0.0    |             |          | 4.9    | 4.6         | 0.3      |
| Halite                        | 0.0    |             |          | 0.0    |             |          | 1.5    | 1.7         | 0.2      |
| Anhydrite                     | 0.0    |             |          | 0.0    |             |          | 14.6   | 14.6        | 0.0      |
| Pyrite                        | 2.5    | 2.4         | 0.1      | 0.0    |             |          | 0.0    |             |          |
| Hematite                      | 0.0    |             |          | 2.5    | 2.4         | 0.1      | 0.0    |             |          |
| Anatase                       | 0.1    | 0.0         | 0.1      | 1.5    | 1.4         | 0.1      | 0.0    |             |          |
| Rutile                        | 0.0    |             |          | 1.5    | 1.2         | 0.3      | 0.0    |             |          |
| Total Non-clay                | 49.4   | 51.5        | 2.9      | 71.1   | 73.2        | 3.1      | 65.3   | 65.8        | 3.3      |
| Kaolinite                     | 16.0   | 15.2        |          | 9.9    | 14.4        |          | 0.0    | 0.1         |          |
| Dickite                       | 0.0    |             |          | 5.5    |             |          | 0.0    |             |          |
| Kaolinite group               | 16.0   | 15.2        | 0.8      | 15.4   | 14.4        | 1.0      | 0.0    | 0.1         | 0.1      |
| Illite 1Mt                    | 10.5   |             |          | 5.5    |             |          | 0.0    |             |          |
| I/S mixed layer               | 10.1   | 25.0        |          | 0.0    | 10.2        |          | 0.0    |             |          |
| Montmorillonite               | 9.5    | 5.0         |          | 0.0    |             |          | 8.0    | 6.3         |          |
| Muscovite 2M1                 | 0.0    |             |          | 5.0    |             |          | 17.1   | 18.4        |          |
| Other dioct. 2:1 phase        | 0.0    |             |          | 0.0    |             |          | 0.0    |             |          |
| Total dioct 2:1 clay and mica | 30.1   | 30.0        | 0.1      | 10.5   | 10.2        | 0.3      | 25.1   | 24.7        | 0.4      |
| Chlorite                      | 4.5    | 3.3         | 1.2      | 3.0    | 2.3         | 0.7      | 9.6    | 9.4         | 0.2      |
| Total clay                    | 50.6   | 48.5        | 2.1      | 28.9   | 26.9        | 2.0      | 34.7   | 34.1        | 0.6      |
| Total identified              | 100.0  | 100.0       | 5.0      | 100.0  | 100.1       | 5.1      | 100.0  | 99.9        | 3.9      |
| Bias non-clay                 |        | 2.9         |          |        | 3.1         |          |        | 3.3         |          |
| Bias clay                     |        | 2.1         |          |        | 2.0         |          |        | 0.6         |          |
| Total bias                    |        | 5.0         |          |        | 5.1         |          |        | 3.9         |          |
| Sum + misidentified           |        |             |          |        | 14.0        |          |        |             |          |

results were collated and a table summarizing how the participants placed in the competition was sent to all active participants. The participants who placed in the top three were informed of their success and invited to attend the annual CMS meeting in order to receive their awards during the conference dinner.

## DISCUSSION

The winner of the 2004 Reynolds Cup showed exceptional skill in quantitative phase analysis by returning a mismatch [*i.e.*  $Abs(W(\text{submitted}) - W(\text{actual}))$ ] of less than 1 wt.% for all but two of the 28 minerals or mineral groups in the three sample mixtures (Table 6). Unfortunately, while these results from the 2004 winner of the Reynolds Cup show just how accurate quantitative phase analysis can be, this was certainly not true of all participants (Figure 3). The contests between 2002 and 2008 showed that a high proportion of participants (~60% in 2002 and ~20% in 2008) were able to quantify the complex synthetic

mixtures to within an average bias per mineral phase (*i.e.* total bias divided by number of phases) of approximately 3 wt.% absolute. Commencing with the 2010 contest, however, less than 10% of participants reported an average bias per mineral phase of 3 wt.% absolute or better. This was primarily because the clay minerals were judged at higher levels of detail. For example prior to 2010, all 2:1 dioctahedral clay minerals (Table 2) were grouped together so that the underestimation of one clay mineral in that group (*e.g.* muscovite 2M<sub>1</sub>) and the overestimation of another (*e.g.* montmorillonite) effectively cancelled out the bias and resulted in a lower overall bias. This was updated in 2010 and subsequent contests by evaluating each of the clay mineral groups individually. As a result, the biases of mainly the clay minerals have increased substantially. A more disturbing trend is the increased number of participants who returned results with total biases that approached or exceeded 300% (Figure 3). This was mainly due to participants who failed to identify mineral phases that were present and more importantly by participants who

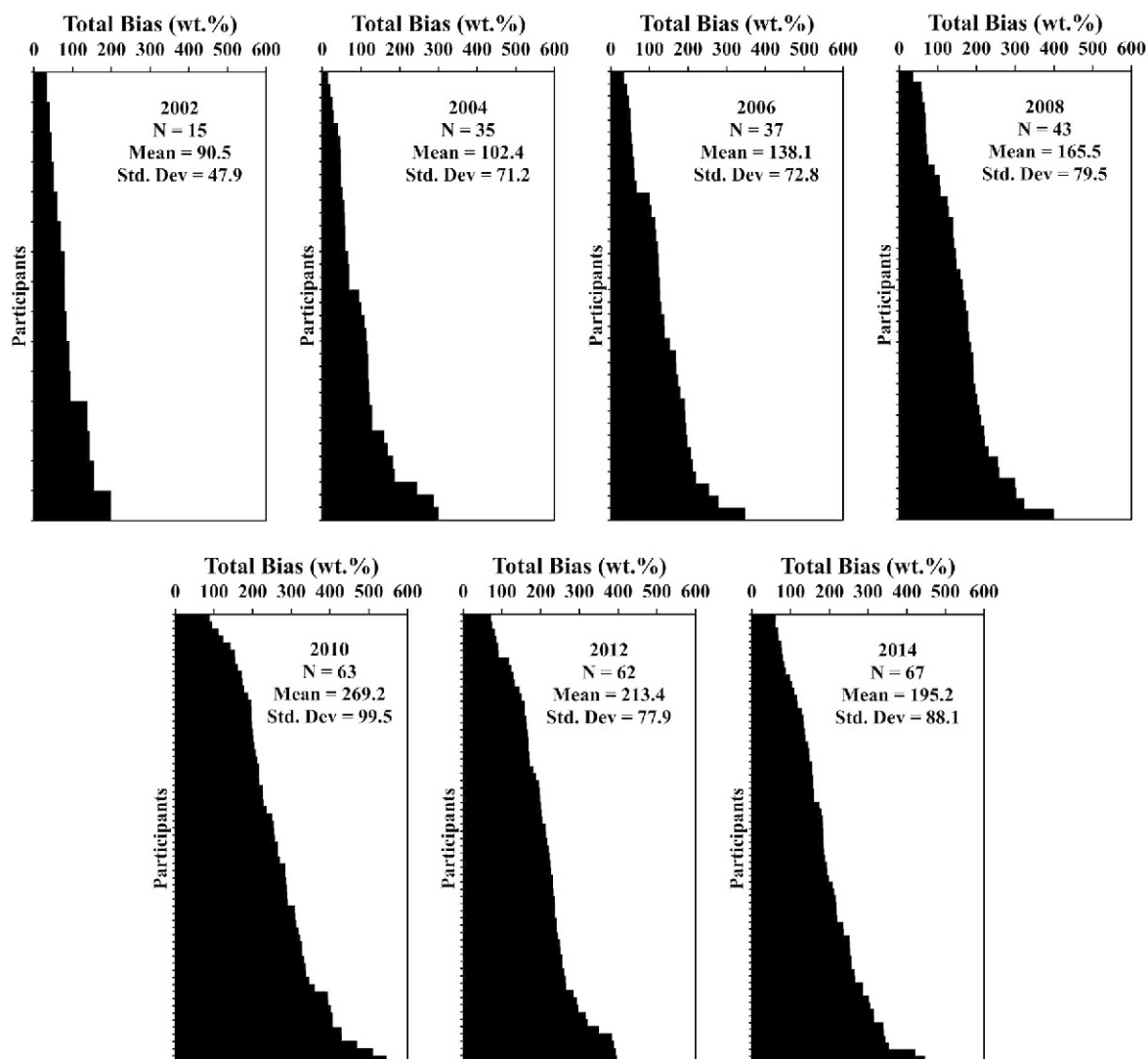


Figure 3. Plots of the total bias for each participant in the 2002, 2004, 2006, 2008, 2010, 2012, and 2014 Reynolds Cup contests plotted using the same total bias scale.

misidentified phases that were not in the samples. Over the course of the seven round robins, more than 300 phases were misidentified. In the 2012 Reynolds Cup, only two of the 62 contestants did not misidentify any phases. In many cases, the misidentification of phases was likely due to the verbatim use of “black box” search-match software. This highlights the importance of accurate qualitative analysis before attempting quantitative analysis. The use of ancillary techniques, in particular clay separations for samples that contained clay minerals was, therefore, of paramount importance in accurate quantitative analysis. Similarly, elemental analyses obtained using XRF or SEM/TEM EDX can be used as constraints to place upper or lower limits on mineralogy or to exclude phases with elemental compositions that do not match the known elemental constituents of a sample. Interestingly, up until the 2014 contest, six different

participants from six different countries were awarded the Reynolds Cup (Table 7). In fact, two previous winners, Steve Hillier and Reinhard Kleeberg, performed at a consistently high standard and placed in the top three in six of the seven Reynolds Cups. The exception was the years that Hillier and Kleeberg organized and prepared the samples for the event. The 2014 Reynolds Cup almost had a tie. Reinhard Kleeberg was awarded first place and Steve Hillier was awarded second place, but both had nearly the same total bias. During the 12 year history of the Reynolds Cup, just 11 participants have shared all 21 of the top three places. These participants all have high levels of expertise in the analysis of clay minerals, which indicates that the appropriate skills and experience are necessary for accurate quantitative clay mineralogy. How can the accuracy and precision of the results returned from all participants of the Reynolds Cup be assessed?



Table 7. Reynolds Cup winners 2002 to 2014.

|  |  |
|--|--|
| 2002   | 2010   |
| 1. Reinhard Kleeberg (Germany)                 | 1. Mark Raven and Peter Self (Australia)   |
| 2. Reiner Dohrmann (Germany)                   | 2. Denny Eberl, Alex Blum, Mario Guzman, Marc Serravezza, and Keith Morrison (USA) |
| 3. Dennis Eberl (USA)                          | 3. Reinhard Kleeberg and Kristian Ufer (Germany)                                   |
| Steve Hillier (Scotland)                       |  |
| 2004   | 2012   |
| 1. Oladipo Omotoso (Canada)                    | 1. Michael Plötze (Switzerland)  |
| 2. Douglas McCarty (USA)                       | 2. Steve Hillier (Scotland)  |
| 3. Steve Hillier (Scotland)                    | 3. Reinhard Kleeberg and Robert Möckel (Germany)                                   |
| Michael Plötze (Switzerland)                   |  |
| 2006   | 2014   |
| 1. Douglas McCarty (USA)                       | 1. Reinhard Kleeberg, Ulf Kempe, and Robert Möckel (Germany)                       |
| 2. Steve Hillier (Scotland)                    | 2. Steve Hillier, Helen Pendlowski, Nia Gray, and Ian Phillips (Scotland)          |
| 3. Reinhard Kleeberg (Germany)                 | 3. Kristian Ufer, Stephan Kaufhold, and Reiner Dohrmann (Germany)                  |
| 2008   | Jan Dietel and Jasmaria Wojatschke (Germany)                                       |
| 1. Steve Hillier (Scotland)                    |  |
| 2. Oladipo Omotoso (Canada)                    |  |
| Reinhard Kleeberg and Kristian Ufer (Germany)  |  |
| 3. Katja Emmerich and Annett Steudel (Germany) |  |
| Steve Chipera (USA)                            |  |
| Dennis Eberl and Alex Blum (USA)               |  |
| Mark Raven (Australia)                         |  |

Furthermore, has there been any improvement in the quantitative analysis of Reynolds Cup samples over the past 12 years? Because the Reynolds Cup is held “in confidence” with only the top three participants identified, it is not possible to gauge whether or not entrants who do not consistently rank in the top three are maintaining or improving their accuracy. The accuracy of the group, however, can be assessed if the percentage of participants that satisfy an accuracy criterion is determined. To assess the accuracy of a quantitative analysis, Calvert *et al.* (1989) stated that in order for an analysis to be defined as “highly accurate” the measured mineral composition should be within 3% absolute or 10% relative of the actual composition. Hillier (2003), in analyzing 239 results from three separate studies, recognized that the criterion of 3% absolute accuracy was overly generous for phases that are present at low concentrations. Based on statistical methods used in the ISO Standard 5725 (ISO, 1994; Hughes and Hurley, 1987), Hillier (2003) suggested that a criterion of  $1/x^n$  where  $x$  is the true concentration and  $n$  is an adjustable number less than 1 was a better measure of accuracy. In the analysis of the accuracy of the Reynolds Cup results, two values of  $n$  have been used: 0.5 to mimic a counting statistics approach and the more stringent value of 0.85, which places tighter limits on the higher concentrations. Plotting the measured versus the actual kaolin composition for the 21 Reynolds Cup samples and the relative error [*i.e.*  $\text{Abs}(W(\text{submitted}) - W(\text{actual})) / W(\text{actual})$ ] versus the actual composition of the same samples illustrates the spread of Reynolds Cup results

(Figures 4a, 4b). Comparing these plots with the  $1/x^n$  criteria described above (Figures 4a, 4b) demonstrates the accuracy of the results submitted for the Reynolds Cup. The solid black lines in Figures 4a, 4b represent the 1:1 composition, the dashed lines the  $\pm 3\%$  limit, the dot-dash lines the  $\pm 1/x^{0.5}$  limit, and the dotted lines the  $\pm 1/x^{0.85}$  limit. It is obvious by the considerable spread in the results that the quantified kaolinite contents from many participants in the Reynolds Cup fall well outside what would be considered accurate. Many participants were unable to identify kaolinite in samples with low amounts, however, several participants failed to identify kaolinite in the higher kaolinite content sample (34.2%) from the Reynolds Cup number 5 in 2010. In this case, halloysite was mixed with disordered kaolinite that was either not identified or was assumed to be just disordered kaolinite. This also reflected the larger than expected underestimation of kaolinite in this sample.

A spread in the results similar to that of kaolinite was found for all other clay minerals in the Reynolds Cup samples. In general, kaolinite, 2:1 dioctahedral clay minerals, serpentine, sepiolite, and palygorskite contents were underestimated, while the contents of 2:1 trioctahedral clay minerals, talc, and chlorite were overestimated. Of the non-clay minerals in the Reynolds Cup samples, the spread in the results for quartz and feldspars was similar to that of kaolinite. The spread in the results for other non-clay minerals in the samples was generally less than kaolinite. For the non-clay minerals, the determined contents for quartz, feldspars, anatase, magnesite, magnetite, gibbsite, amphiboles, rutile, and

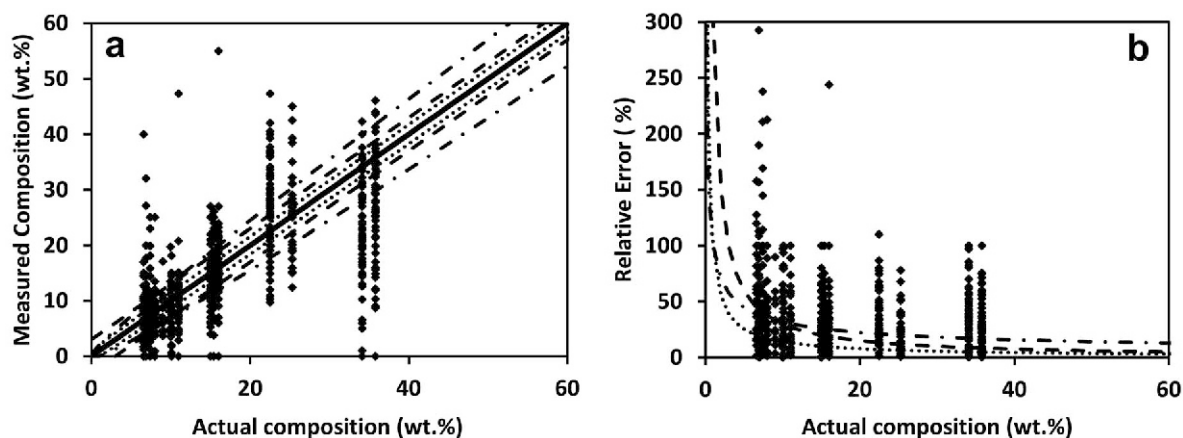


Figure 4. Plots of (a) the measured vs. the actual composition and (b) the relative error vs. the actual composition of kaolinite for all participants. The solid line indicates a 1:1 correspondence between measured and actual composition, dash lines a  $\pm 3\%$  absolute bias, the dot-dashed lines the  $\pm 1/x^{0.5}$  limit, and the dotted lines the  $\pm 1/x^{0.85}$  limit where  $x$  is the true concentration.

gypsum were more often overestimated, while the contents of the other non-clay minerals were mostly underestimated. The non-crystalline content of the samples was often not identified by participants. When the non-crystalline content was identified, the amount of non-crystalline material was usually overestimated. In order to evaluate if, as a group, participants were improving or not, the percentages of the participants in each Reynolds Cup who met the accuracy criteria for kaolinite clay minerals, 2:1 dioctahedral clay minerals, and quartz were plotted (Figure 5). Overall improvements as a group would result in an increase in the percentage of participants that achieved the selected criteria. In general terms, the percentage of participants that met each of the accuracy criteria since 2004 has remained steady during the last decade of the Reynolds Cup competition. Only 15 participants returned results for the 2002 contest so these data are not statistically valid. During the 10 year period, however, the complexity of the samples to be analyzed has increased and the method of assessing the bias of submitted results has been tightened (*i.e.* greater emphasis was placed on the quantification of individual clay mineral types). Consequently, on the basis of increased complexity and a tightening of the criteria for assessing clay minerals, it may be said that there has been an overall improvement in the ability of laboratories to analyze the increasingly complex samples of the Reynolds Cup competition. The spread in the accuracies (*i.e.* total biases) of the returned results, however, has remained large (Figure 3). If only the biases of participants who placed in the top 10% (*i.e.* had biases in the lowest 10% of total biases from all participants) are considered, then from 2002 to 2008 (Reynolds Cup 1 to Reynolds Cup 4) both the total bias and the bias for clay minerals remained relatively constant. In 2010 (Reynolds Cup 5), there was a large jump in both the total bias and the bias for clay minerals for the participants who placed in the

top 10%. This jump is attributed to the changes in the method of evaluating the bias for clay minerals (and therefore the total bias) that occurred in 2010. Since 2010, there has been a steady decrease in the total bias and the bias for clay minerals of the participants who placed in the top 10%. In the 2014 competition (Reynolds Cup 7), the total bias and the bias for clay minerals of these participants had almost returned to pre-2010 levels. This is indicative of the concerted effort that in recent years has been put into the quantitative analysis of clay mineral content by powder X-ray diffraction.

## CONCLUSIONS

Over the first twelve years of the Reynolds Cup competition, there have been seven contests to analyze 21 synthetic sample mixtures that closely approximate clay and clay mineral assemblages found in nature. These 21 samples contained a wide variety of minerals including clay minerals from eight clay mineral groups as well as 39 non-clay minerals. There have been a total of 448 participants or group participants from more than 25 countries with several participants that took part in nearly all contests. The approximately 14,000 analyses that have been carried out as part of the Reynolds Cup have provided a comprehensive database of the accuracy of a wide range of techniques (but in particular powder XRD) as the techniques are applied by various laboratories to quantify the mineral contents of clay and clay mineral assemblages. Quantification of the results from the participants that placed in the top 10 in each of the Reynolds Cup competitions show that clay and clay mineral assemblages can be quantified to a very high degree of accuracy. It is notable that a number of laboratories have consistently placed highly in the Reynolds Cup competitions. There have been 27 participants that placed in the top three to date in the

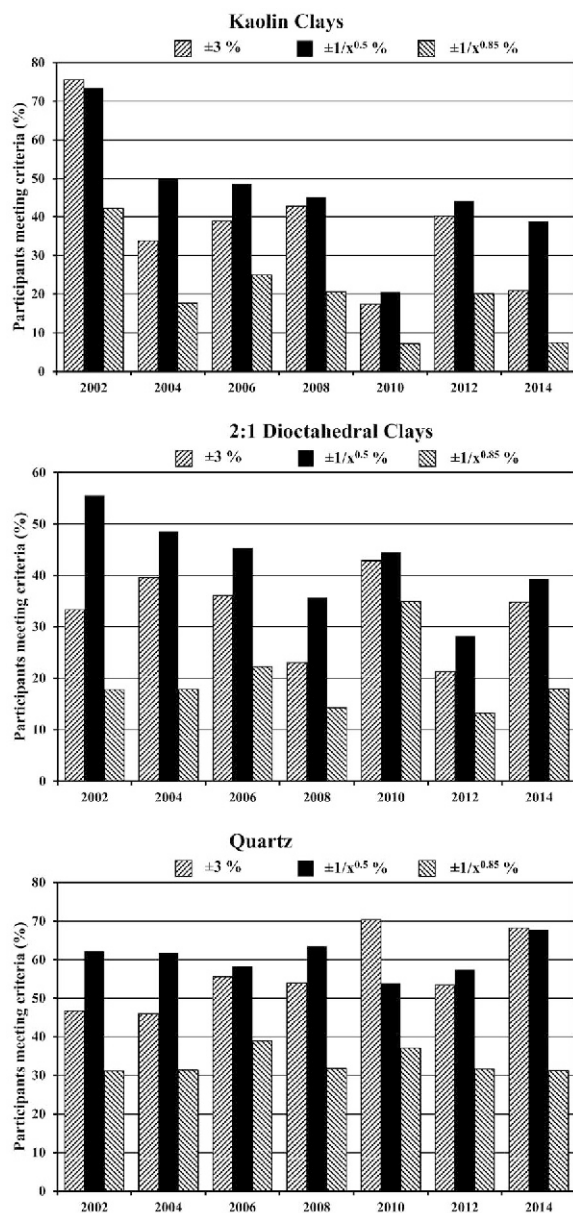


Figure 5. Plots of the percentage of participants that met the accuracy criterion for kaolin clay minerals, 2:1 dioctahedral clay minerals, and quartz which showed a  $\pm 3\%$  absolute bias, a  $\pm 1/x^{0.5}$  limit, and a  $\pm 1/x^{0.85}$  limit where  $x$  is the true concentration. Results for the 2002 contest are probably unreliable due to the low number of returned results (15).

12 year history of the Reynolds Cup and all of these top placements in the competition were shared by just 11 participants or participant groups (<http://www.clays.org/society%20awards/rcresults.html>). These laboratories tend to be those that specialize in the analysis of clays and clay minerals and are at the forefront of technique development. The laboratories often, but not always, used several ancillary techniques to fully characterize the samples. At the other extreme, many laboratories do

very poorly in the quantification of clay and clay mineral assemblages. Because the entrants of the Reynolds Cup competition are asked to provide details of their methods, the competition provides insights into the common sources of error in quantitative analyses. These sources of error are apparent in all stages of a quantitative analysis. Surprisingly, many of these sources of error are thought to be “well known” and the procedures for avoiding errors are well documented (see for example Moore and Reynolds, 1997; Zevin and Kimmel, 1995). Poor sample preparation (e.g. failure to prepare suitably sized particles through techniques such as micronizing) can lead to unreliable results particularly for phases present in minor amounts. Similarly, the need to separate out clay-sized fractions and prepare oriented films that are subjected to various treatments is often essential in the identification and quantification of clay minerals. The correct identification of phases highlights the paradigm that the first step in an accurate quantitative analysis is a good qualitative analysis. Throughout the Reynolds Cup competition there are numerous examples where phases have been identified and purportedly quantified when in fact the identified phases are totally unrealistic for the particular sample, but presumably the phases have been identified through the unquestioned use of automated search-match software. A second likely cause of inaccurate quantification is inappropriate instrument settings for the samples being analyzed. The Reynolds Cup competitions showed that it is necessary to optimize instrument settings over a wide range of recording conditions. For example, XRD patterns of 2:1 sheet silicates require an instrument capable of obtaining reliable measurements at both low and high angles. Consequently it may be necessary to use a range of instrument settings, such as automatic divergence slits or fixed divergence slits with variable counting times to obtain the optimum data for quantitative analysis. The 12 years of the Reynolds Cup have seen a marked increase in the availability and sophistication of software for the quantitative analysis of clay minerals. The Reynolds Cup competition has demonstrated that a wide variety of analytical software is capable of producing a highly accurate quantification of clay and clay-mineral assemblages. The Rietveld method is the most popular technique of choice among participants, which is also reflected in the number of successful participants who gained the top three places and indeed the ultimate winners. The competition has also shown that participants using the same software can produce some extraordinarily bad results when used incorrectly or inappropriately. This is certainly the case for participants who used the Rietveld method with an overly large proportion of the worst performers using this technique. The Reynolds Cup competition has over an extended period of time provided an invaluable database for assessing the accuracy of powder diffraction techniques for the quantification of clay and clay

mineral assemblages. Future Reynolds Cup competitions will continue to be a gauge of the current state of quantification by XRD and will, to some extent, drive the development of new analytical methods and the testing of these methods in “real world” situations.

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