

# Accuracy in quantitative phase analysis of complex mineral assemblages: A decade of Reynolds Cup round robins

Mark D Raven and Peter G Self  
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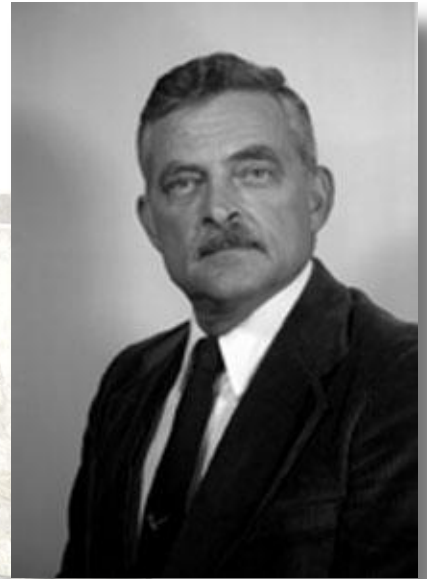
# Outline

- The Reynolds Cup
- Sample Compositions
- Analytical techniques
- Quantitative analysis methods
- Summary
- Conclusions



# The Reynolds Cup

- Biennial competition named after Bob Reynolds
- Established in 2000 by The Clay Minerals Society and sponsored by ChevronTexaco and the USGS
- Utilizes three sample mixtures of pure mineral phases that represent realistic sedimentary and weathered rock compositions
- Open to anyone interested in quantitative mineralogy using any available technique
- Commences early in the even numbered years
- Deadline approximately 1 month before the annual meeting of the CMS



# The Reynolds Cup (cont)

- Entrants are judged on sample biases

$$TotalBias = \sum abs(W_{actual} - W_{submitted})$$

- Top three with the lowest total bias are awarded with plaques and the winner receives the perpetual Reynolds Cup trophy
- Winner is invited to prepare samples for the next contest



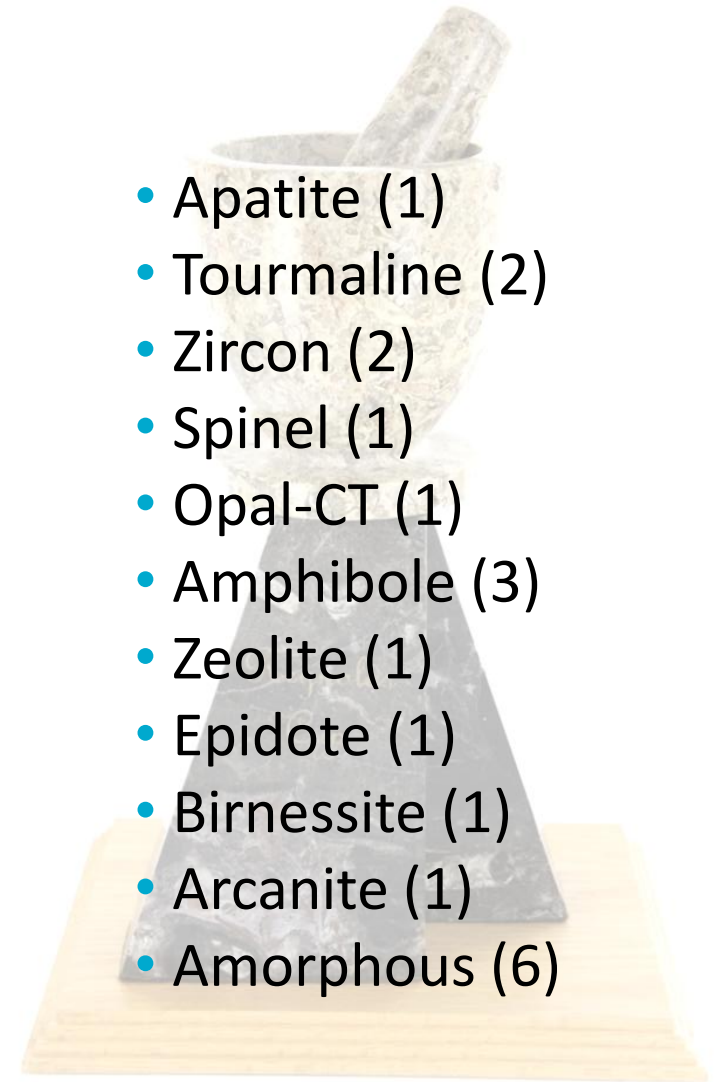
# Sample compositions

- Mudstone
- Sandstone
- Siltstone
- Calcareous mudstone
- Saline sedimentary rock
- Sediment from an evaporate environment
- Sample representing a hydrothermal alteration environment
- Soil formed on a parent material rich in ferromagnesian minerals and amorphous soil minerals
- Petroleum shale
- Nickel laterite
- Bauxite



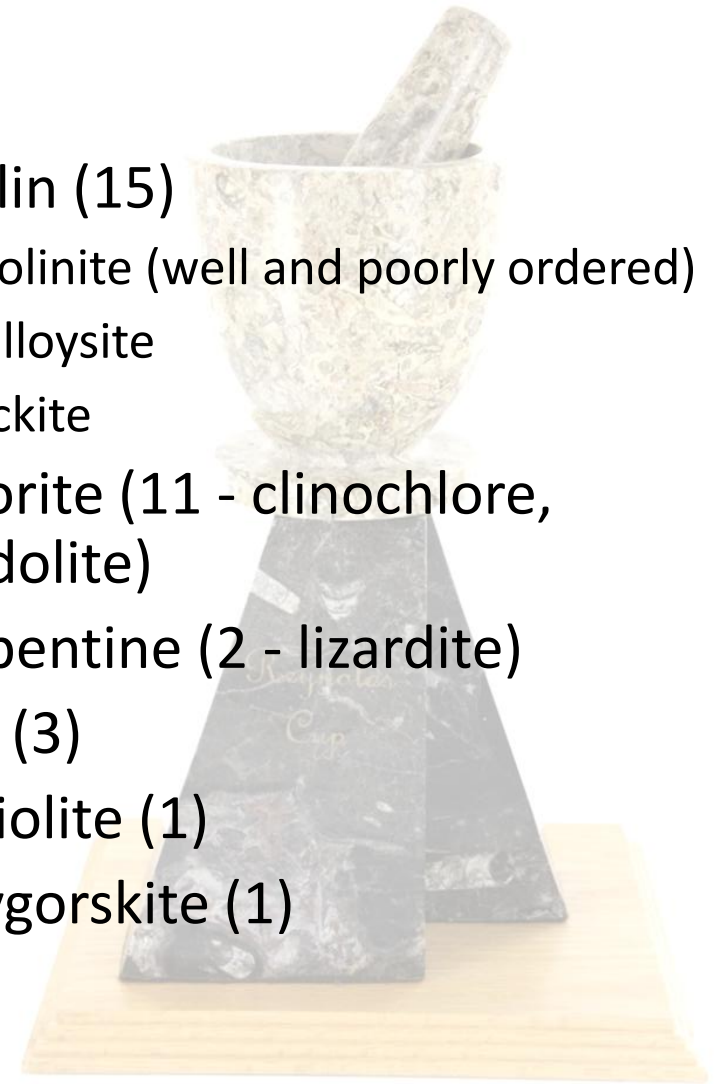
# Minerals used – non clays

- Quartz (18)
- K-feldspar (13)
- Plagioclase (14)
- Calcite (12)
- Dolomite (10)
- Magnesite (4)
- Aragonite (3)
- Huntite (1)
- Halite (6)
- Pyrite (7)
- Siderite (8)
- Barite (5)
- Gypsum (2)
- Anhydrite (2)
- Alunite (1)
- Hematite (6)
- Goethite (5)
- Magnetite (4)
- Anatase (9)
- Rutile (3)
- Ilmenite (3)
- Gibbsite (3)
- Bohmite (1)
- Fluorite (2)
- Apatite (1)
- Tourmaline (2)
- Zircon (2)
- Spinel (1)
- Opal-CT (1)
- Amphibole (3)
- Zeolite (1)
- Epidote (1)
- Birnessite (1)
- Arcanite (1)
- Amorphous (6)



# Minerals used – clays

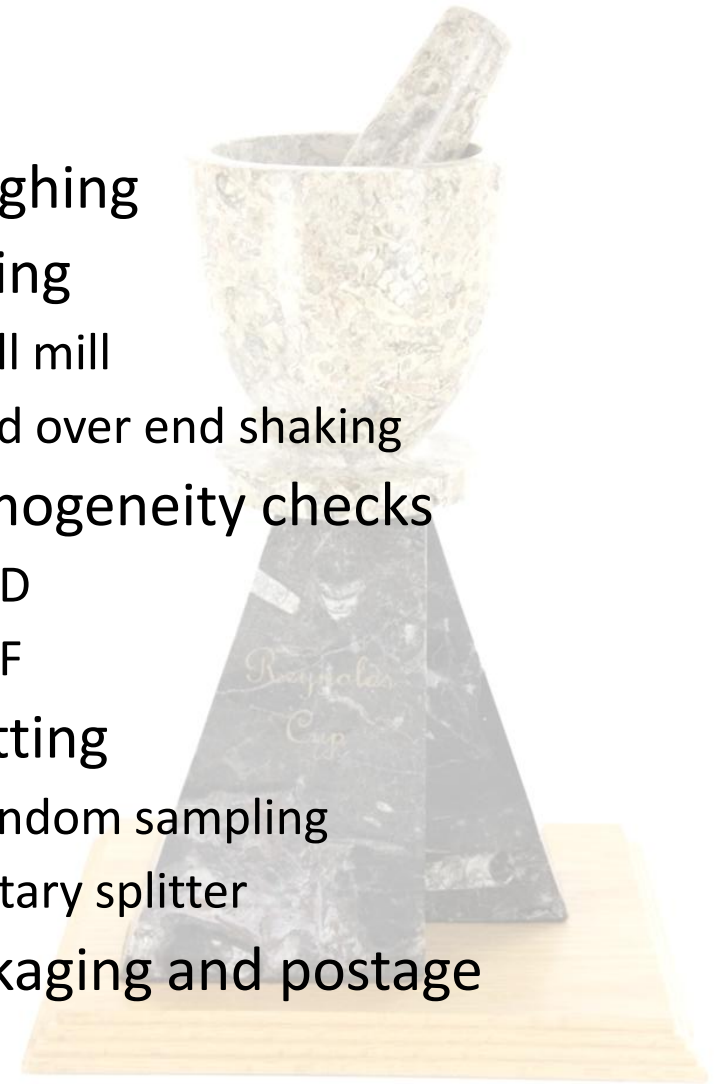
- 2:1 Dioctahedral Clays (18)
  - Smectite (montmorillonite, nontronite)
  - Mixed layered (illite-smectite, glauconite-smectite)
  - Mica/Illite (muscovite  $2M_1$ , illite  $1M_d$ ,  $1M$ )
- 2:1 Trioctahedral Clays (6)
  - Smectite (saponite)
  - Vermiculite
  - Mixed layered (corrensite)
  - Mica (biotite)
- Kaolin (15)
  - Kaolinite (well and poorly ordered)
  - Halloysite
  - Dickite
- Chlorite (11 - clinochlore, ripidolite)
- Serpentine (2 - lizardite)
- Talc (3)
- Sepiolite (1)
- Palygorskite (1)





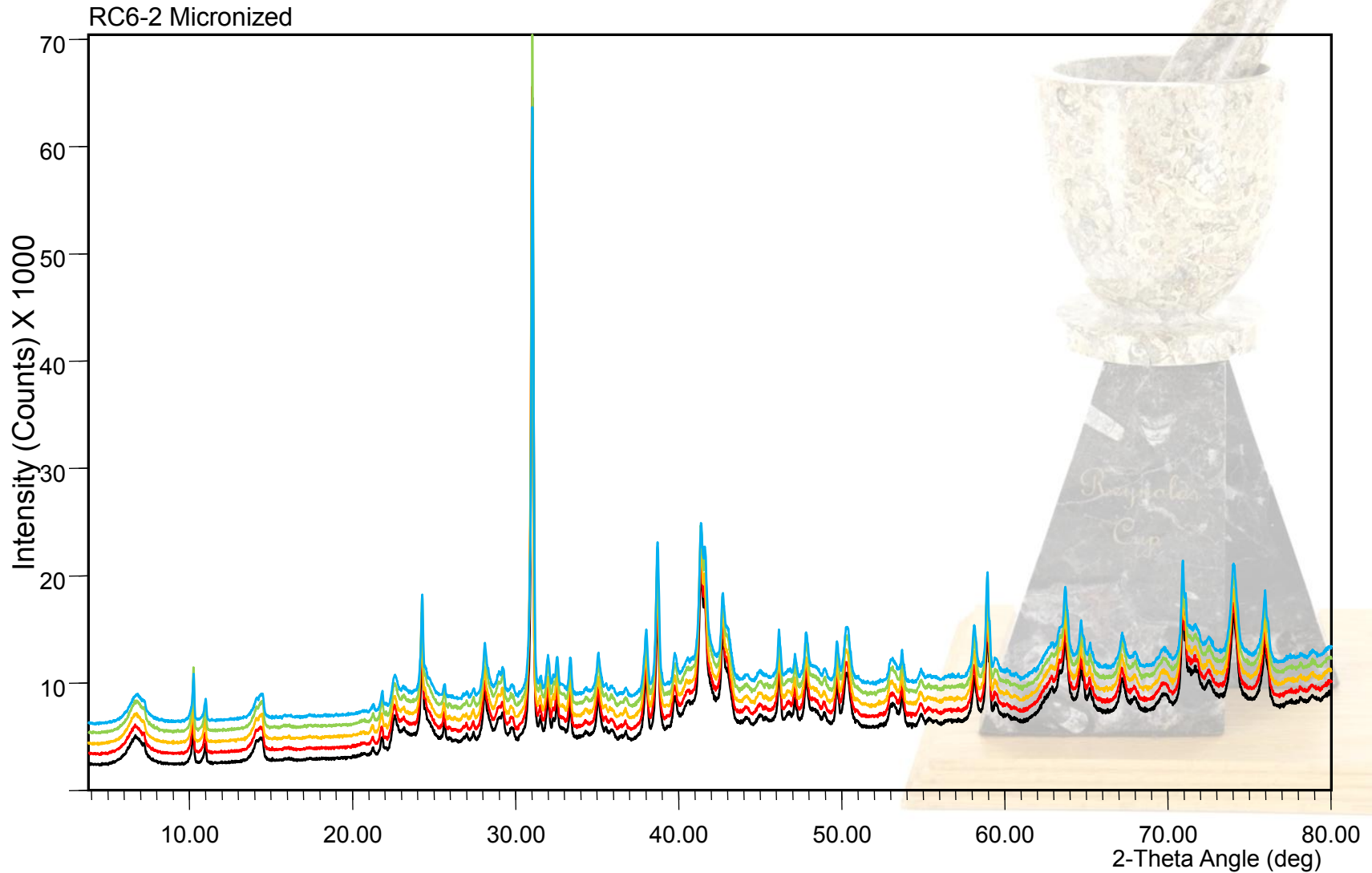
# Sample preparation

- Purification
  - Hand picking
  - Sieving
  - Magnetic separation
  - Chemical treatments
  - Size fractionation (<2 $\mu\text{m}$ , <0.5 $\mu\text{m}$ , <0.2 $\mu\text{m}$ )
  - Synthesis
- Preparation
  - Grinding
  - Sieving (200-400 $\mu\text{m}$ )
  - Check for purity (XRD)
- Equilibrate
- Weighing
- Mixing
  - Ball mill
  - End over end shaking
- Homogeneity checks
  - XRD
  - XRF
- Splitting
  - Random sampling
  - Rotary splitter
- Packaging and postage



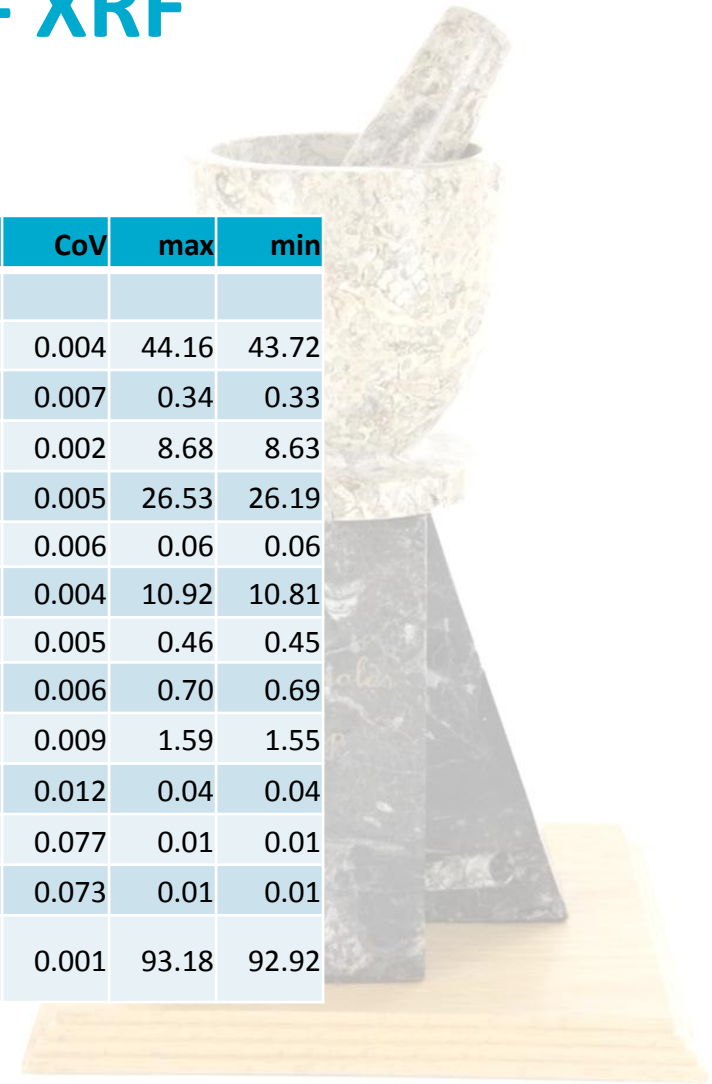


# Homogeneity check RC6-2 - XRD

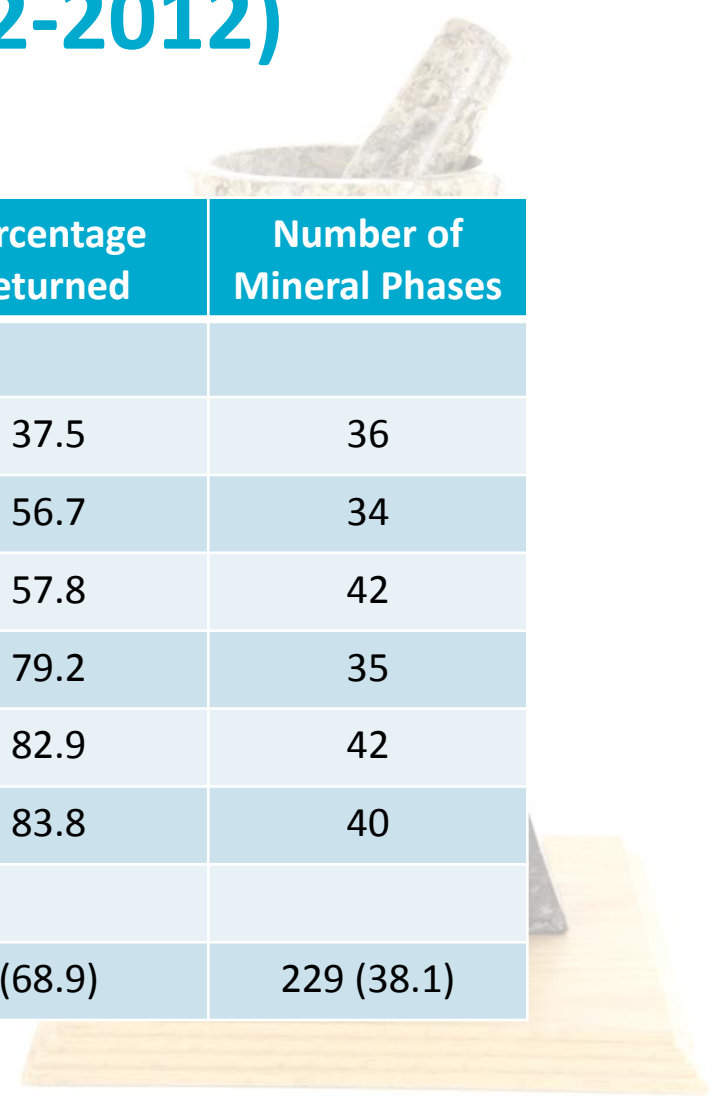


# Homogeneity check RC6-2 - XRF

|                                |     | 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 |



# Round robin statistics (2002-2012)



| 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                       |
| Total (mean) | 367 (61.2)   | 253 (42.3)       | (68.9)              | 229 (38.1)               |

# Reynolds Cup Winners (2002-2012)

- **2002**

1. **Reinhard Kleeberg (Germany)**
2. Reiner Dohrmann (Germany)
3. Dennis Eberl (USA)  
Steve Hillier (Scotland)

- **2004**

1. **Oladipo Omotoso (Canada)**
2. Douglas McCarty (USA)
3. Steve Hillier (Scotland)  
Michael Plötze (Switzerland)

- **2006**

1. **Douglas McCarty (USA)**
2. Steve Hillier (Scotland)
3. Reinhard Kleeberg (Germany)

- **2008**

1. **Steve Hillier (Scotland)**
2. Oladipo Omotoso (Canada)  
Reinhard Kleeberg and Kristian Ufer (Germany)
3. Katja Emmerich & Annett Steudel (Germany)  
Steve Chipera (USA)  
Dennis Eberl & Alex Blum (USA)  
Mark Raven (Australia)

- **2010**

1. **Mark Raven and Peter Self (Australia)**
2. Denny Eberl, Alex Blum, Mario Guzman, Marc Serravezza and Keith Morrison (USA)
3. Reinhard Kleeberg and Kristian Ufer (Germany)

- **2012**

1. **Michael Plötze (Switzerland)**
2. Steve Hillier (Scotland)
3. Reinhard Kleeberg and Robert Möckel (Germany)



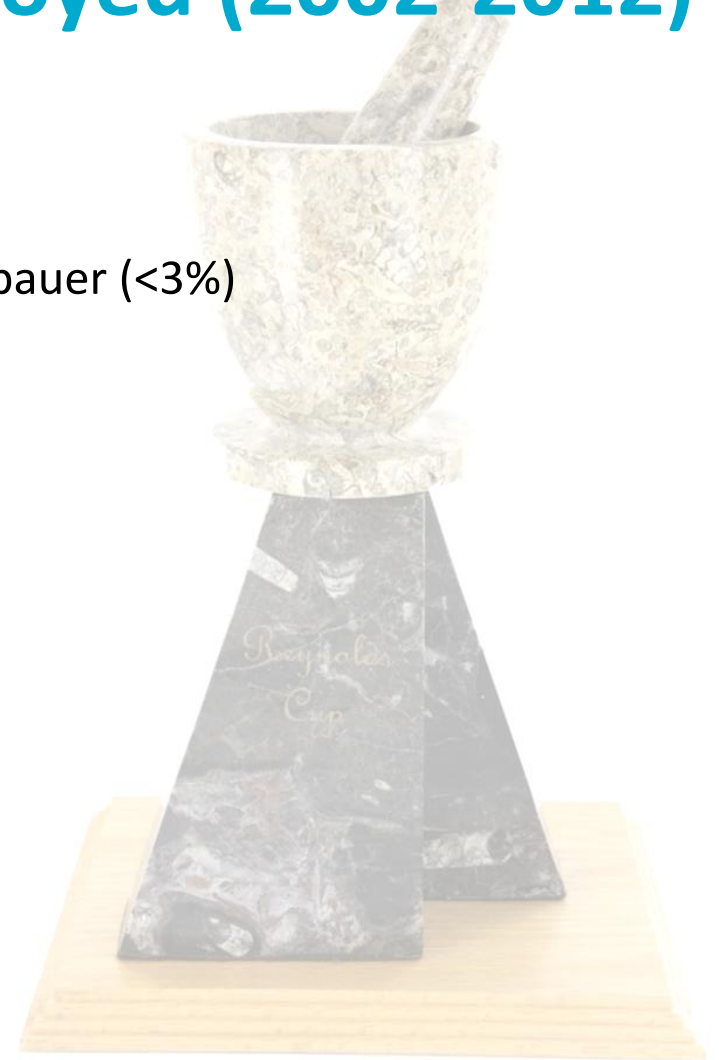
# Participants of the 2012 Reynolds Cup

- 74 registrants
- 25 countries
  - Australia (4)
  - Belgium (1)
  - Canada (1)
  - China (1)
  - Colombia (2)
  - Denmark (1)
  - France (6)
  - Germany (11)
  - Greece (2)
  - Hungary (1)
  - India (1)
  - Italy (1)
  - Kenya (1)
  - Korea (1)
  - Norway (1)
  - Poland (2)
  - Russia (6)
  - Saudi Arabia (2)
  - Slovakia (1)
  - South Africa (1)
  - Spain (2)
  - Switzerland (1)
  - Turkey (3)
  - United Kingdom (6)
  - United States of America (15)



# Analytical techniques employed (2002-2012)

- Primary quantification technique
  - XRD (>97%)
  - IR, FT-IR, Raman spectroscopy, SEM/TEM, Mossbauer (<3%)
- Ancillary techniques
  - Chemical analysis (XRF, ICP, neutron activation)
  - FT-IR, VNIR reflectance
  - DTA-TGA-DSC
  - Electron microscopy (SEM/TEM-EDX)
  - Wet chemistry
  - CEC
  - Carbonate analysis
  - Surface area
  - Optical microscopy, petrography
  - Mossbauer
  - Ion chromatography



# XRD techniques (2002-2012)

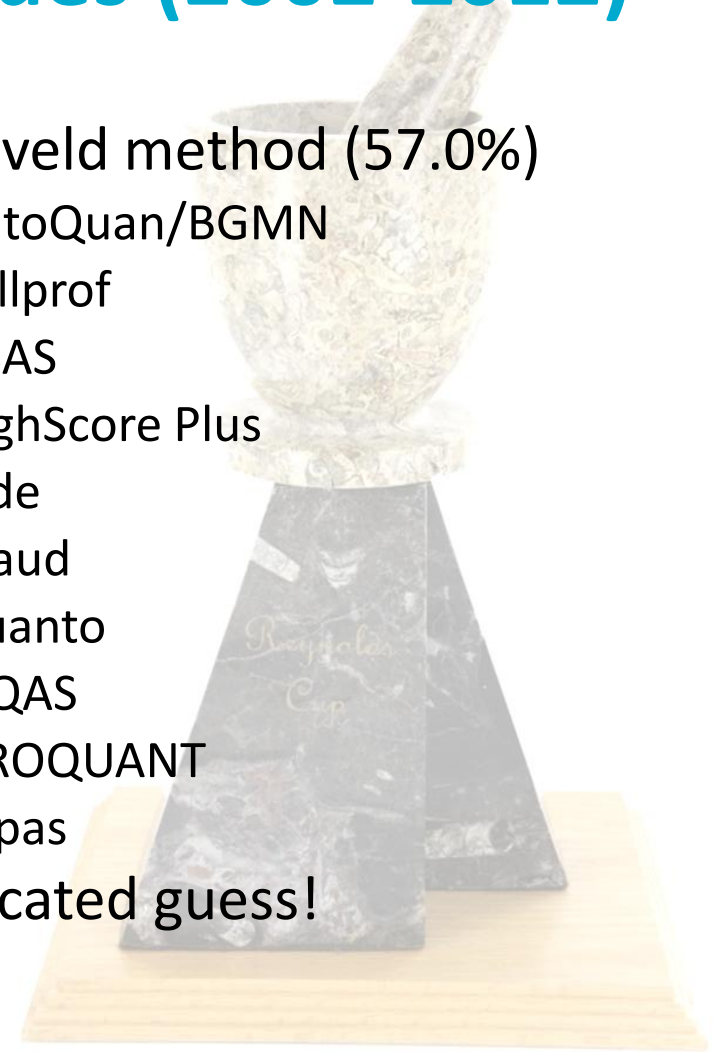
- Bulk pressed powders
- Magnetic fraction
- Optical separation
- Grain size separation
  - Sieving
  - Dispersion and sedimentation
- Oriented samples
  - Cation saturations
  - Heating
  - Ethylene glycol/glycerol solvation





# XRD quantification techniques (2002-2012)

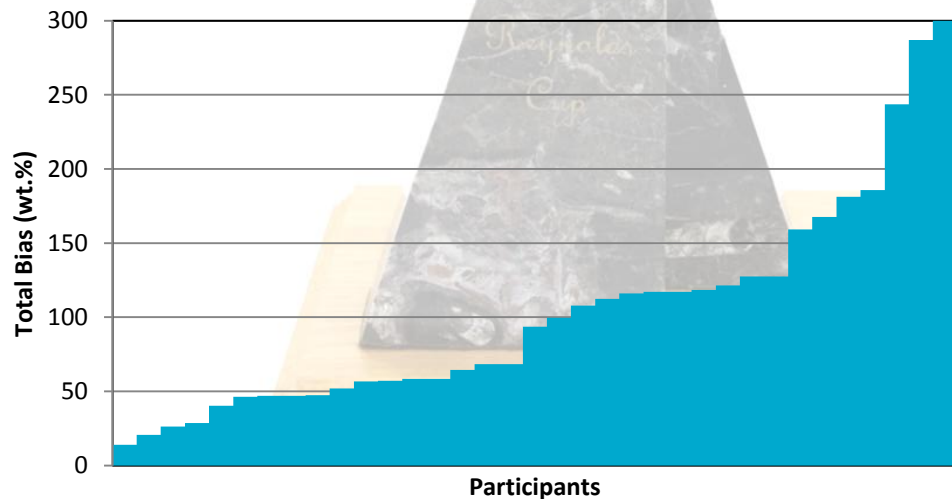
- Single peak methods (21.0%)
  - Matrix flushing
  - NEWMOD
  - RIR ICDD-PDF
- Whole pattern techniques (19.5%)
  - Arquant
  - Fullpat
  - Hillier
  - Quanta
  - Rancourt and Dang
  - RockJock
  - X-LS Mineral
- Rietveld method (57.0%)
  - AutoQuan/BGMN
  - Fullprof
  - GSAS
  - HighScore Plus
  - Jade
  - Maud
  - Quanto
  - RIQAS
  - SIROQUANT
  - Topas
- Educated guess!



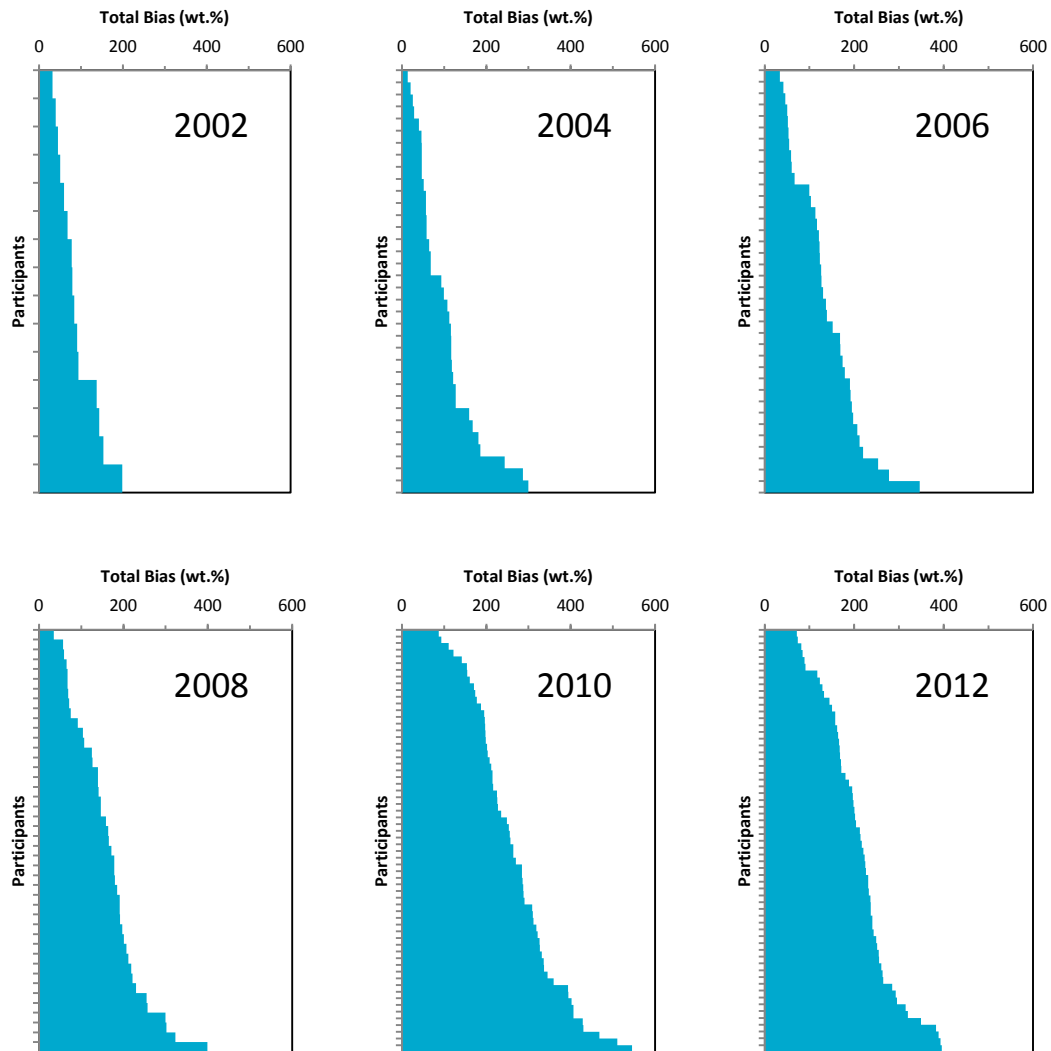
# Results (2004)

| Mineral                              | RC2-1(wt.%) |             |     | RC2-2(wt.%) |             |     | RC2-3(wt.%) |             |     |
|--------------------------------------|-------------|-------------|-----|-------------|-------------|-----|-------------|-------------|-----|
|                                      | (wt.%)      | Adj. (wt.%) | Δ   | (wt.%)      | Adj. (wt.%) | Δ   | (wt.%)      | Adj. (wt.%) | Δ   |
| <b>Quartz</b>                        | 24.8        | 25.1        | 0.3 | 45.7        | 47.0        | 1.3 | 14.7        | 14.8        | 0.1 |
| <b>K-Feldspar</b>                    | 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         |             |     |
| other plagioclase                    | 0.0         |             |     | 0.0         |             |     | 0.0         |             |     |
| <b>Plagioclase</b>                   | 6.5         | 8.3         | 1.8 | 10.7        | 11.7        | 1.0 | 2.9         | 3.7         | 0.8 |
| <b>Calcite</b>                       | 5.0         | 5.3         | 0.3 | 0.0         | 0.0         | 0.0 | 18.6        | 17.7        | 0.9 |
| Dolomite                             | 2.0         |             |     | 0.0         |             |     | 6.0         |             |     |
| Ankerite                             | 0.0         |             |     | 0.0         |             |     | 0.0         |             |     |
| <b>Dolomite</b>                      | 2.0         | 2.1         | 0.1 | 0.0         | 0.0         | 0.0 | 6.0         | 5.8         | 0.2 |
| <b>Magnesite</b>                     | 0.0         | 0.0         | 0.0 | 0.0         | 0.0         | 0.0 | 4.9         | 4.6         | 0.3 |
| <b>Halite</b>                        | 0.0         | 0.0         | 0.0 | 0.0         | 0.0         | 0.0 | 1.5         | 1.7         | 0.2 |
| <b>Anhydrite</b>                     | 0.0         | 0.0         | 0.0 | 0.0         | 0.0         | 0.0 | 14.6        | 14.6        | 0.0 |
| <b>Pyrite</b>                        | 2.5         | 2.4         | 0.1 | 0.0         | 0.0         | 0.0 | 0.0         | 0.0         | 0.0 |
| <b>Hematite</b>                      | 0.0         | 0.0         | 0.0 | 2.5         | 2.4         | 0.1 | 0.0         | 0.0         | 0.0 |
| <b>Anatase</b>                       | 0.1         | 0.1         | 0.0 | 1.5         | 1.4         | 0.1 | 0.0         | 0.0         | 0.0 |
| <b>Rutile</b>                        | 0.0         | 0.0         | 0.0 | 1.5         | 1.2         | 0.3 | 0.0         | 0.0         | 0.0 |
| <b>Total Non-clay</b>                | 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         |             |     |
| <b>Kaolinite group</b>               | 16.0        | 15.2        | 0.8 | 15.4        | 14.4        | 1.0 | 0.0         | 0.0         | 0.0 |
| 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         |             |     |
| <b>Total dioct 2:1 clay and mica</b> | 30.1        | 30.0        | 0.1 | 10.5        | 10.2        | 0.3 | 25.1        | 24.7        | 0.4 |
| <b>Chlorite</b>                      | 4.5         | 3.3         | 1.2 | 3.0         | 2.3         | 0.7 | 9.6         | 9.4         | 0.2 |
| <b>Total clay</b>                    | 50.6        | 48.5        | 2.1 | 28.9        | 26.9        | 2.0 | 34.7        | 34.1        | 0.6 |
| <b>Total identified</b>              | 100.0       | 100.0       | 5.0 | 100.0       | 100.1       | 5.1 | 100.0       | 99.9        | 3.9 |
| <b>Bias non-clay</b>                 |             | 2.9         |     |             | 3.1         |     |             | 3.3         |     |
| <b>Bias clay</b>                     |             | 2.1         |     |             | 2.0         |     |             | 0.6         |     |
| <b>Total bias</b>                    |             | 5.0         |     |             | 5.1         |     |             | 3.9         |     |
| <b>Sum + Misidentified</b>           |             |             |     |             | 14.0        |     |             |             |     |

| Nr | Participant | Total bias RC2/1 | Total bias RC2/2 | Total bias RC2/3 | Sum bias |
|----|-------------|------------------|------------------|------------------|----------|
| 1  | 19          | 5.00             | 5.10             | 3.90             | 14.00    |
| 2  | 13          | 7.20             | 4.80             | 8.60             | 20.60    |
| 3  | 1           | 13.60            | 8.20             | 4.50             | 26.30    |
| 4  | 15          | 3.60             | 12.20            | 12.90            | 28.70    |
| 5  | 3           | 15.00            | 6.30             | 19.00            | 40.30    |
| 6  | 17          | 13.70            | 15.00            | 17.70            | 46.40    |
| 7  | 57          | 17.00            | 16.60            | 13.40            | 47.00    |
| 8  | 47          | 15.00            | 15.00            | 17.10            | 47.10    |
| 9  | 42          | 15.80            | 10.80            | 20.80            | 47.40    |
| 10 | 29          | 22.20            | 16.00            | 13.80            | 52.00    |

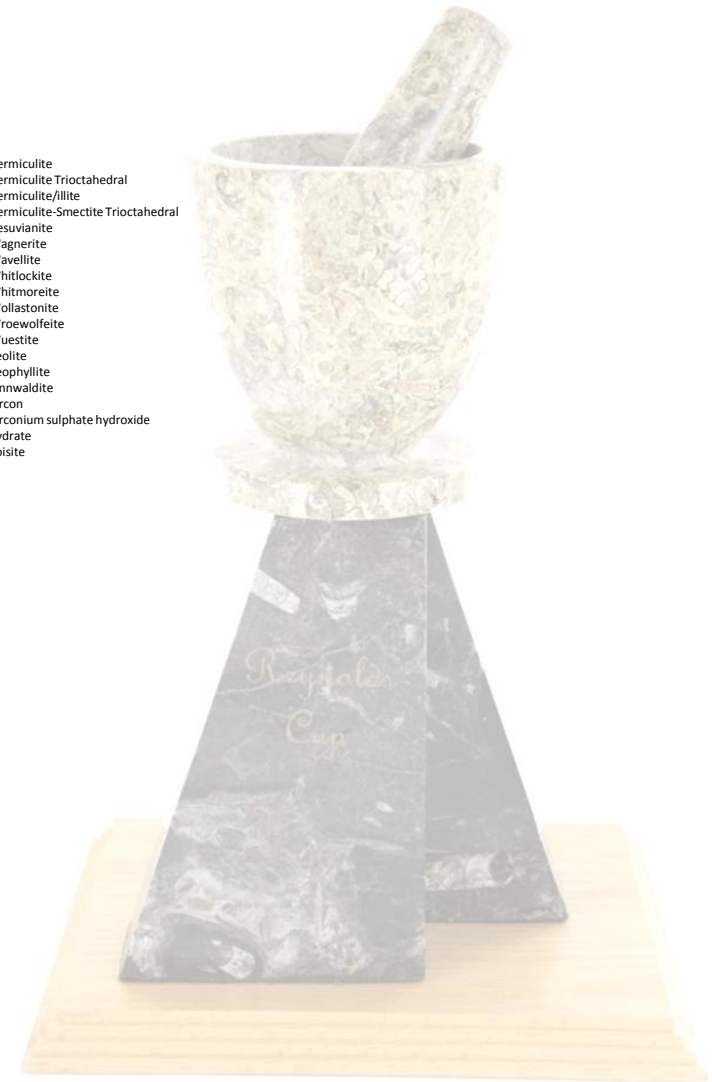


# Total biases for all contests (2002-2012)



# Misidentified phases

|                                   |                            |                                   |                                   |  |
|-----------------------------------|----------------------------|-----------------------------------|-----------------------------------|--|
| • Actinolite                      | • Chrysotile               | • Ilmenite                        | • Phlogopite (2M1 )               | • Vermiculite                          |
| • Aegerine                        | • Clinocllore              | • iterstratified (tri)            | • Phlogopite (mica-trioctahedral) | • Vermiculite Trioctahedral            |
| • Aerinite                        | • Clinoenstate             | • Iron                            | • phosphate hydrate               | • Vermiculite/illite                   |
| • Akaganeite                      | • Clinoptilolite           | • Iron Silicon                    | • Plagioclase                     | • Vermiculite-Smectite Trioctahedral   |
| • Albite/anorthite                | • ClinoPyroxene            | • Jarosite                        | • Portlandite                     | • Vesuvianite                          |
| • Allophane                       | • Clinozoisite             | • KAlSiO4                         | • Potarite                        | • Wagnerite                            |
| • Alluaudite                      | • Cordierite               | • Kaolinite                       | • Prehnite                        | • Wavellite                            |
| • Almandine                       | • Corrensite               | • kaolinite/smectite              | • Pseudobrookite                  | • Whitlockite                          |
| • Al-Mg                           | • Corundum                 | • kaolinite-Chlorite              | • Pumpellyite                     | • Whitmoreite                          |
| • AlO                             | • Cotunnite                | • K-feldspar                      | • Pyrite                          | • Wollastonite                         |
| • Alumina gamma                   | • Cristobalite             | • Kieserite                       | • Pyrolusite                      | • Wroewolfeite                         |
| • Aluminite                       | • Cryptohalite             | • K-rich Chlorite                 | • pyrophyllite 1T                 | • Wuestite                             |
| • Alunite                         | • Crysofile                | • Kutnohorite                     | • pyrophyllite 2M                 | • Zeolite                              |
| • Alunogen                        | • Diaspore                 | • Laueite                         | • Pyroxene                        | • Zeophyllite                          |
| • Amorphous                       | • Dickite                  | • Laumonite                       | • Pyroxene (Augite)               | • Zinnwaldite                          |
| • Amorphous (Allophane)           | • Dickite/Nacrite          | • Lepidocrocite                   | • Pyroxene (Ferroan Diopside)     | • Zircon                               |
| • Amorphous KAISi3O8              | • Diopside                 | • Leucite                         | • Pyrrhotite                      | • Zirconium sulphate hydroxide hydrate |
| • Amorphous Si                    | • Dolomite                 | • Lime                            | • Rectortite                      | • Zoisite                              |
| • Amorphous SiO2                  | • Dolomite/Ankerite        | • Lithosite                       | • Reyerite                        |  |
| • Amorphous Volcanic Glass        | • Elpidite                 | • Lizardite                       | • Rhodochrosite                   |  |
| • Amphibole                       | • Enstatite                | • Magnesioferrite                 | • Rhodonite                       |  |
| • Analcime                        | • Epidote                  | • Magnesite                       | • Rodolicoite                     |  |
| • Anatase                         | • Euclase                  | • Magnetite                       | • Rutile                          |  |
| • Andesine                        | • Faujasite                | • Malachite                       | • Sanidine                        |  |
| • Anhydrite                       | • Fe oxide                 | • Manganite                       | • Saponite                        |  |
| • Ankerite                        | • Fedorite                 | • Melantenite                     | • Saucornite                      |  |
| • Anorthite                       | • Feldspar (Kspar)         | • MgZn3                           | • Schorl                          |  |
| • Antigorite                      | • Ferrhydrite              | • Mg-calcite                      | • Sepiolite                       |  |
| • Antlerite                       | • Ferrite magnesian        | • MgSO4                           | • Serpentine                      |  |
| • Apatite                         | • Fluorapatite             | • Mica                            | • Siderite                        |  |
| • Aragonite                       | • Forsterite               | • Mica Trioctahedral              | • Siderite (Mn-rich)              |  |
| • Arcanite                        | • Galeite                  | • Mica-Vermiculite Trioctahedral  | • Siderite(not Mg)                |  |
| • Arsenolite As2O3                | • Garnet                   | • Microcline                      | • Silicon                         |  |
| • Augite                          | • Gehlenite                | • Missing                         | • Silicon dioxide                 |  |
| • Barite                          | • Gibbsite                 | • Monazite                        | • Sillimanite                     |  |
| • Bazalt                          | • Gismondine               | • Monohydrocalcite                | • Smectite trioctahedral          |  |
| • Berthierine                     | • Glass/Obsidian           | • Montmorillonite (Tri)           | • Smithsonite                     |  |
| • Biotite                         | • Glauberite               | • Moschellandsbergite             | • Sodalite                        |  |
| • Birnessite                      | • Glauconite               | • Mullite                         | • Spenceite                       |  |
| • Bromcarnallite                  | • Goethite                 | • Nacrite                         | • Sphalerite iron                 |  |
| • Brookite                        | • Gypsum                   | • Na-Feldspar                     | • Spinel                          |  |
| • Brucite                         | • Halite                   | • Natrolite                       | • Stauriolite                     |  |
| • Brushite                        | • Halite potassian         | • Nepheline                       | • Strontianite                    |  |
| • Bytownite                       | • Halloysite               | • Nitride Silicon                 | • Sylvite                         |  |
| • C6H5O3P2Zn                      | • Hectonite                | • Nordstrandite                   | • Syngenite                       |  |
| • Calcite                         | • Hedenbergite             | • Norrishite                      | • Szomolnokite                    |  |
| • CaMg2Al16O27                    | • Hematite                 | • Oligoclase                      | • Talc                            |  |
| • Carbonate-fluorapatite          | • Hercynite                | • Olivine                         | • Thenardite                      |  |
| • Carnallite                      | • Heulandite               | • Opal                            | • Thermanatrite                   |  |
| • CaSiO3                          | • Hexahydrite              | • Opal CT                         | • Titanite                        |  |
| • Celestine                       | • Hornblende               | • Orthoclase                      | • Titanomagnetite                 |  |
| • Chabazite                       | • Hotsonite                | • OrthoPyroxene                   | • Tobermorite                     |  |
| • Chalcosite                      | • Hyalophane               | • Osumilite                       | • Tourmaline                      |  |
| • Chlorargyrite                   | • hydrated Ca-Mg carbonate | • Others not precisely identified | • Trimerite                       |  |
| • Chlorite Dioctahedral           | • Hydrocalumite            | • oxide 1                         | • Trydimite                       |  |
| • Chlorite Trioctahedral          | • Hydrotalcite             | • oxide 2                         | • Tungstite                       |  |
| • Chlorite-Montmorillonite(Tri)   | • Hydroxylapatite          | • Palygorskite                    | • Unidentified                    |  |
| • Chlorite-Smectite Trioctahedral | • Hydroxylapatite          | • Periclase                       | • Unnamed hydrate                 |  |
| • Chlorite-vermiculite            | • Hypersthene              | • Perovskite                      | • Vaterite                        |  |
| • Chromite                        | • Illite Tri               | • Phillipsite                     | • Vauxite                         |  |



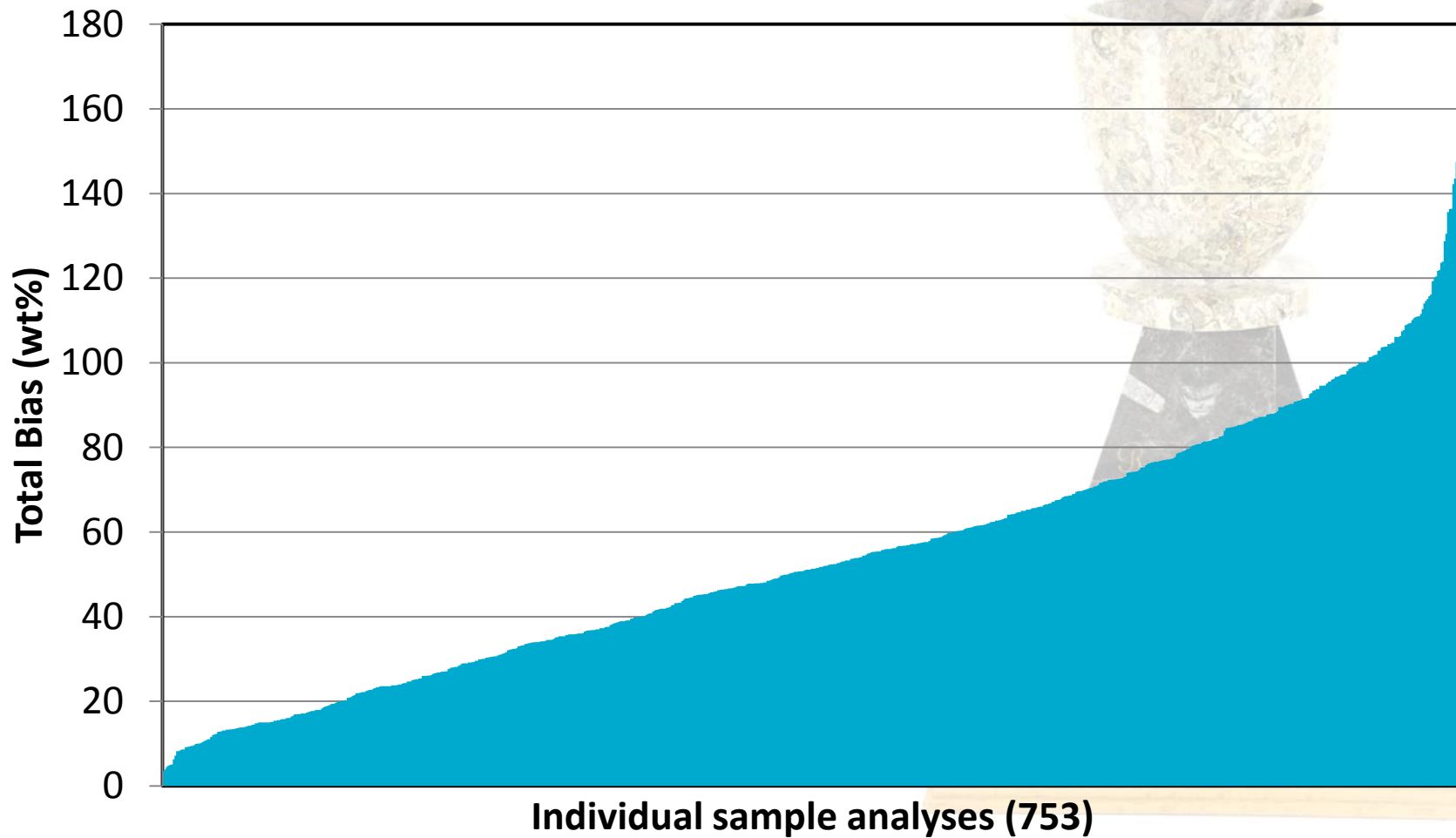
# Misidentified phases

|                                   |                            |                                   |                                   |  |
|-----------------------------------|----------------------------|-----------------------------------|-----------------------------------|--|
| • Actinolite                      | • Chrysotile               | • Ilmenite                        | • Phlogopite (2M1 )               | • Vermiculite                          |
| • Aegerine                        | • Clinocllore              | • iterstratified (tri)            | • Phlogopite (mica-trioctahedral) | • Vermiculite Trioctahedral            |
| • Aerinite                        | • Clinoenstate             | • Iron                            | • phosphate hydrate               | • Vermiculite/illite                   |
| • Akaganeite                      | • Clinoptilolite           | • Iron Silicon                    | • Plagioclase                     | • Vermiculite-Smectite Trioctahedral   |
| • Albite/anorthite                | • ClinoPyroxene            | • Jarosite                        | • Portlandite                     | • Vesuvianite                          |
| • Allophane                       | • Clinozoisite             | • KAlSiO4                         | • Potarite                        | • Wagnerite                            |
| • Alluaudite                      | • Cordierite               | • Kaolinite                       | • Prehnite                        | • Wavellite                            |
| • Almandine                       | • Corrensite               | • kaolinite/smectite              | • Pseudobrookite                  | • Whitlockite                          |
| • Al-Mg                           | • Corundum                 | • kaolinite-Chlorite              | • Pumpellyite                     | • Whitmoreite                          |
| • AlO                             | • Cotunnite                | • K-feldspar                      | • Pyrite                          | • Wollastonite                         |
| • Alumina gamma                   | • Cristobalite             | • Kieserite                       | • Pyrolusite                      | • Wroewolfeite                         |
| • Aluminite                       | • Cryptohalite             | • K-rich Chlorite                 | • pyrophyllite 1T                 | • Wuestite                             |
| • Alunite                         | • Crysofile                | • Kutnohorite                     | • pyrophyllite 2M                 | • Zeolite                              |
| • Alunogen                        | • Diaspore                 | • Laueite                         | • Pyroxene                        | • Zeophyllite                          |
| • Amorphous                       | • Dickite                  | • Laumonite                       | • Pyroxene (Augite)               | • Zinnwaldite                          |
| • Amorphous (Allophane)           | • Dickite/Nacrite          | • Lepidocrocite                   | • Pyroxene (Ferroan Diopside)     | • Zircon                               |
| • Amorphous KAISi3O8              | • Diopside                 | • Leucite                         | • Pyrrhotite                      | • Zirconium sulphate hydroxide hydrate |
| • Amorphous Si                    | • Dolomite                 | • Lime                            | • Rectortite                      | • Zoisite                              |
| • Amorphous SiO2                  | • Dolomite/Ankerite        | • Lithosite                       | • Reyerite                        |  |
| • Amorphous Volcanic Glass        | • Elpidite                 | • Lizardite                       | • Rhodochrosite                   |  |
| • Amphibole                       | • Enstatite                | • Magnesioferrite                 | • Rhodonite                       |  |
| • Analcime                        | • Epidote                  | • Magnesite                       | • Rodolicoite                     |  |
| • Anatase                         | • Euclase                  | • Magnetite                       | • Rutile                          |  |
| • Andesine                        | • Faujasite                | • Malachite                       | • Sanidine                        |  |
| • Anhydrite                       | • Fe oxide                 | • Manganite                       | • Saponite                        |  |
| • Ankerite                        | • Fedorite                 | • Melantenite                     | • Saucornite                      |  |
| • Anorthite                       | • Feldspar (Kspar)         | • MgZn3                           | • Schorl                          |  |
| • Antigorite                      | • Ferrhydrite              | • Mg-calcite                      | • Sepiolite                       |  |
| • Antlerite                       | • Ferrite magnesian        | • MgSO4                           | • Serpentine                      |  |
| • Apatite                         | • Fluorapatite             | • Mica                            | • Siderite                        |  |
| • Aragonite                       | • Forsterite               | • Mica Trioctahedral              | • Siderite (Mn-rich)              |  |
| • Arcanite                        | • Galeite                  | • Mica-Vermiculite Trioctahedral  | • Siderite(not Mg)                |  |
| • Arsenolite As2O3                | • Garnet                   | • Microcline                      | • Silicon                         |  |
| • Augite                          | • Gehlenite                | • Missing                         | • Silicon dioxide                 |  |
| • Barite                          | • Gibbsite                 | • Monazite                        | • Sillimanite                     |  |
| • Bazalt                          | • Gismondine               | • Monohydrocalcite                | • Smectite trioctahedral          |  |
| • Berthierine                     | • Glass/Obsidian           | • Montmorillonite (Tri)           | • Smithsonite                     |  |
| • Biotite                         | • Glauberite               | • Moschellandsbergite             | • Sodaite                         |  |
| • Birnessite                      | • Glauconite               | • Mullite                         | • Spencerite                      |  |
| • Bromcarnallite                  | • Goethite                 | • Nacrite                         | • Sphalerite iron                 |  |
| • Brookite                        | • Gypsum                   | • Na-Feldspar                     | • Spinel                          |  |
| • Brucite                         | • Halite                   | • Natrolite                       | • Stauriolite                     |  |
| • Brushite                        | • Halite potassium         | • Nepheline                       | • Strontianite                    |  |
| • Bytownite                       | • Halloysite               | • Nitride Silicon                 | • Sylvite                         |  |
| • C6H5O3P2Zn                      | • Hectonite                | • Nordstrandite                   | • Syngenite                       |  |
| • Calcite                         | • Hedenbergite             | • Norrishite                      | • Szomolnokite                    |  |
| • CaMg2Al16O27                    | • Hematite                 | • Oligoclase                      | • Talc                            |  |
| • Carbonate-fluorapatite          | • Hercynite                | • Olivine                         | • Thenardite                      |  |
| • Carnallite                      | • Heulandite               | • Opal                            | • Thermanatrite                   |  |
| • CaSiO3                          | • Hexahydrite              | • Opal CT                         | • Titanite                        |  |
| • Celestine                       | • Hornblende               | • Orthoclase                      | • Titanomagnetite                 |  |
| • Chabazite                       | • Hotsonite                | • OrthoPyroxene                   | • Tobermorite                     |  |
| • Chalcosite                      | • Hyalophane               | • Osumilite                       | • Tourmaline                      |  |
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| • Chlorite-Smectite Trioctahedral | • Hydroxylapatite          | • Periclase                       | • Unnamed hydrate                 |  |
| • Chlorite-vermiculite            | • Hyperthene               | • Perovskite                      | • Vaterite                        |  |
| • Chromite                        | • Illite Tri               | • Phillipsite                     | • Vauxite                         |  |



260!

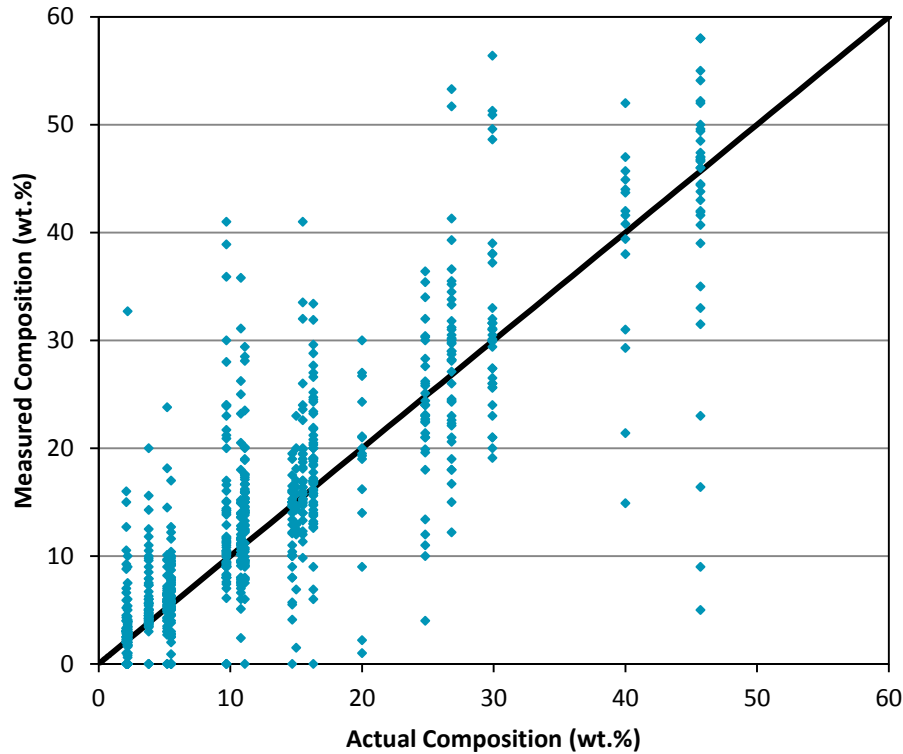
# Bias for all participants and all samples (2002-2012)



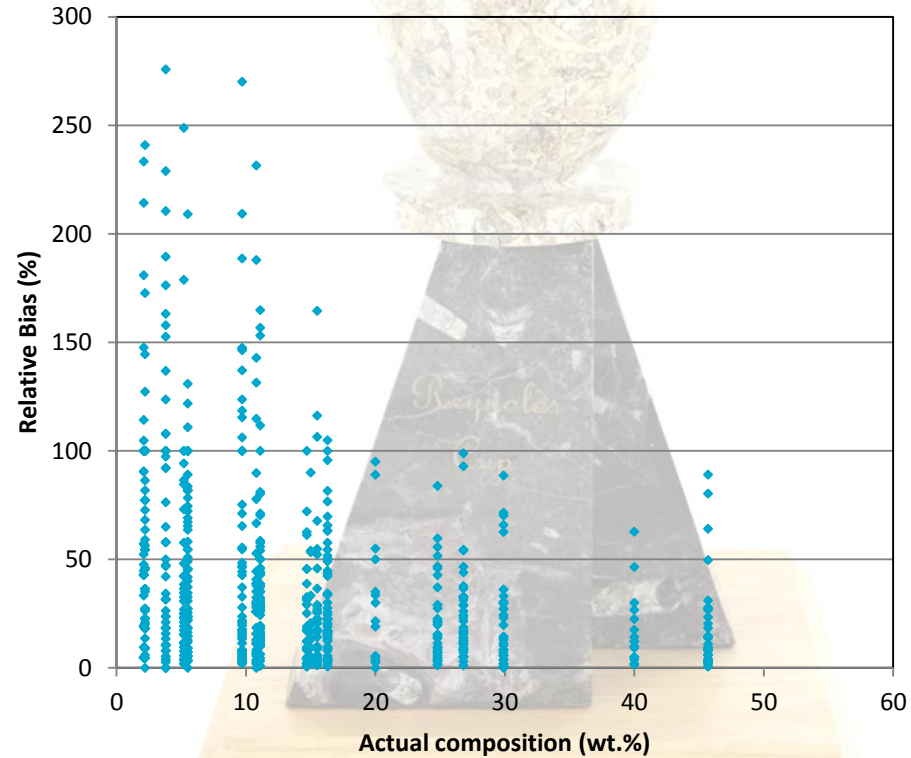
# How is accuracy quantified?

## Quartz

Absolute Bias (wt.%)



Relative Bias (%)

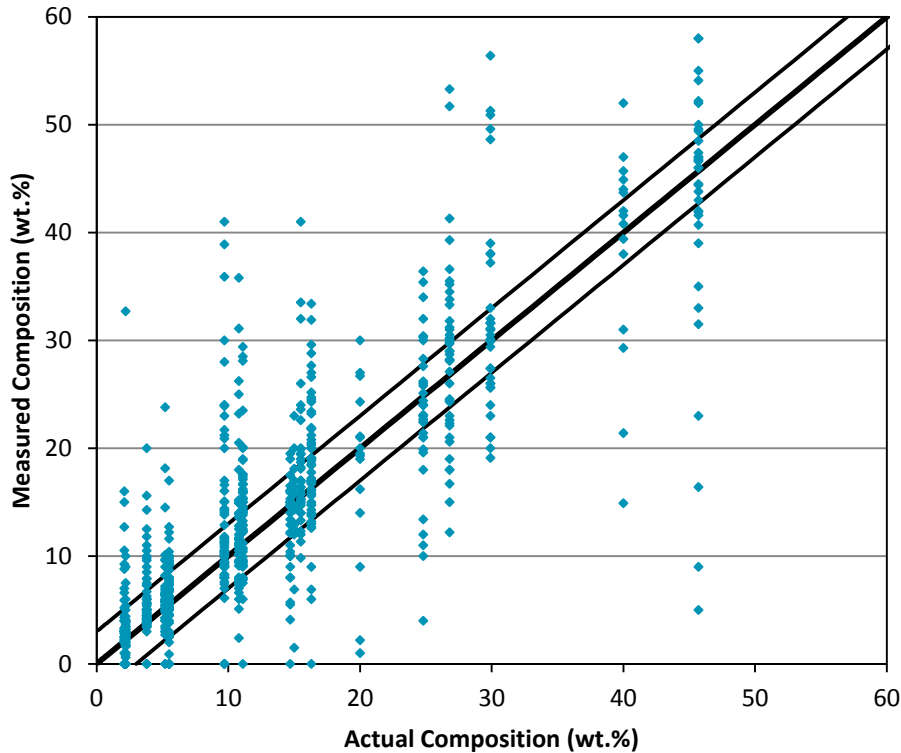




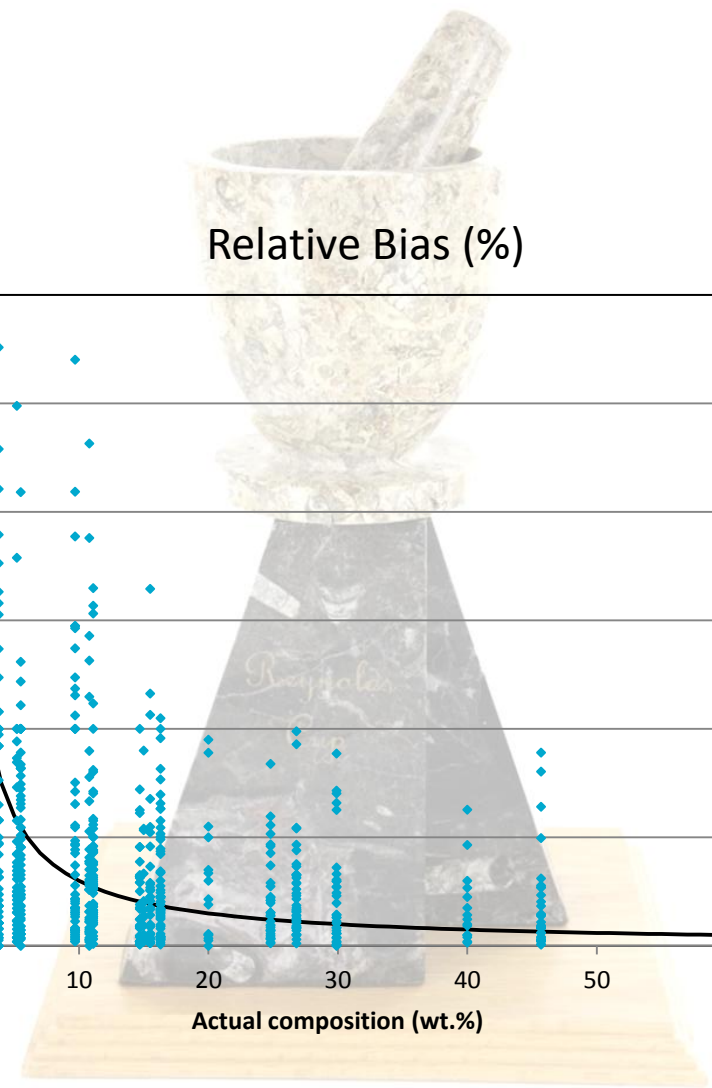
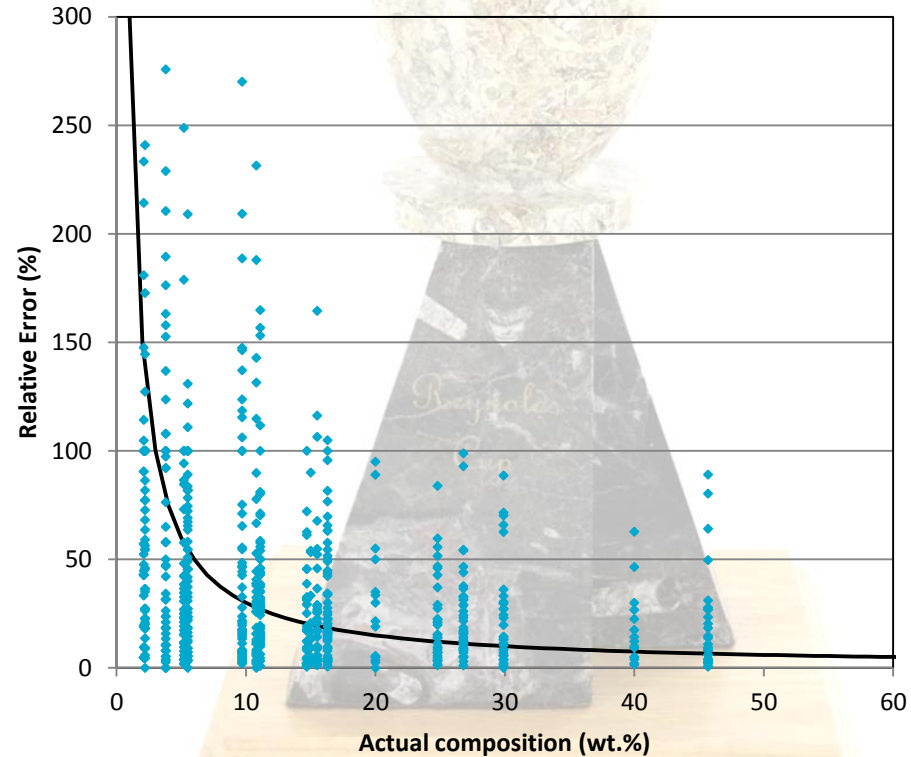
# Quartz – $\pm 3\%$ absolute bias

Analyses that meet the criteria: 423 (56.2%)

Absolute Bias (wt.%)



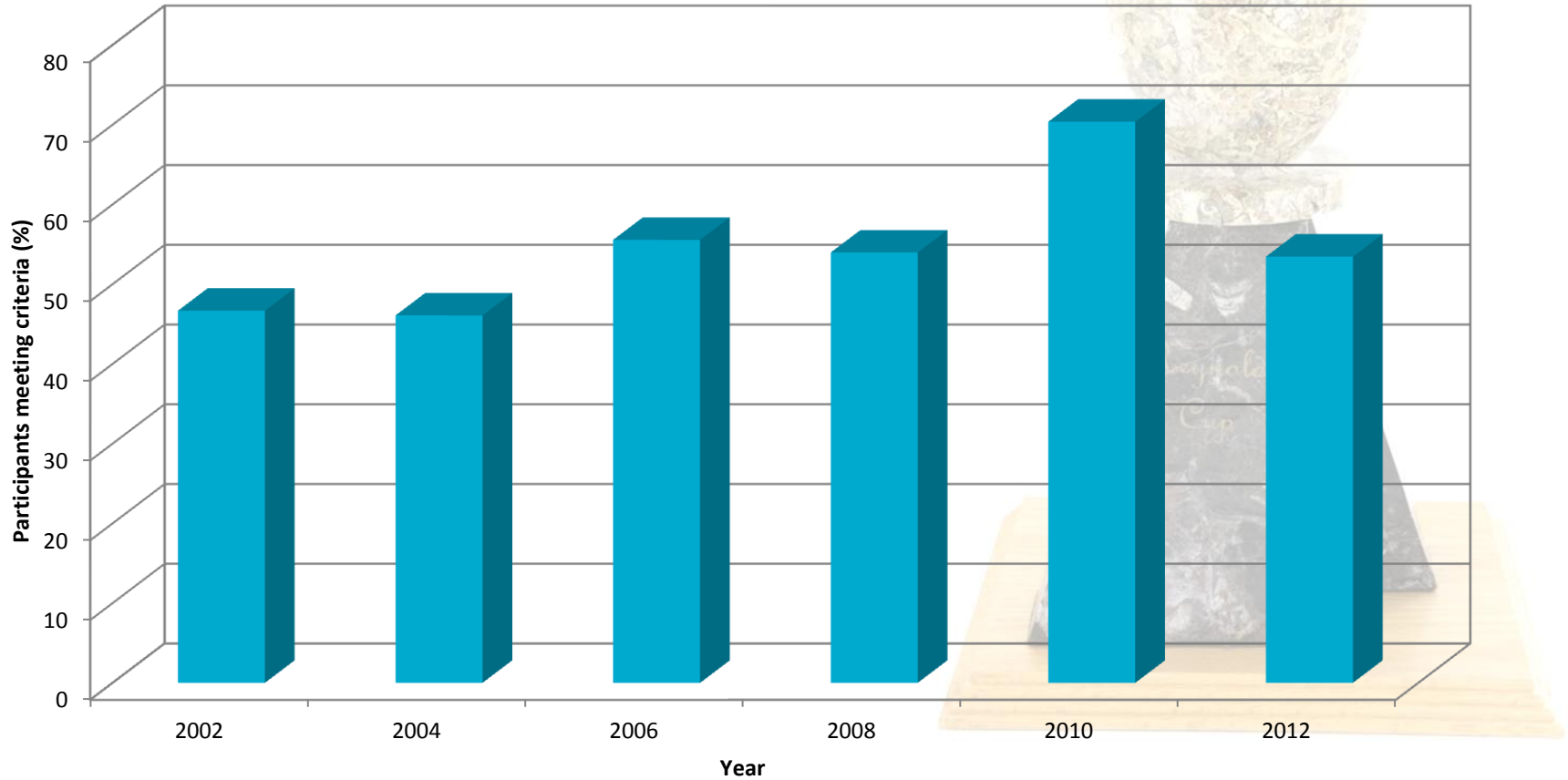
Relative Bias (%)



# Are we there yet?

## Quartz

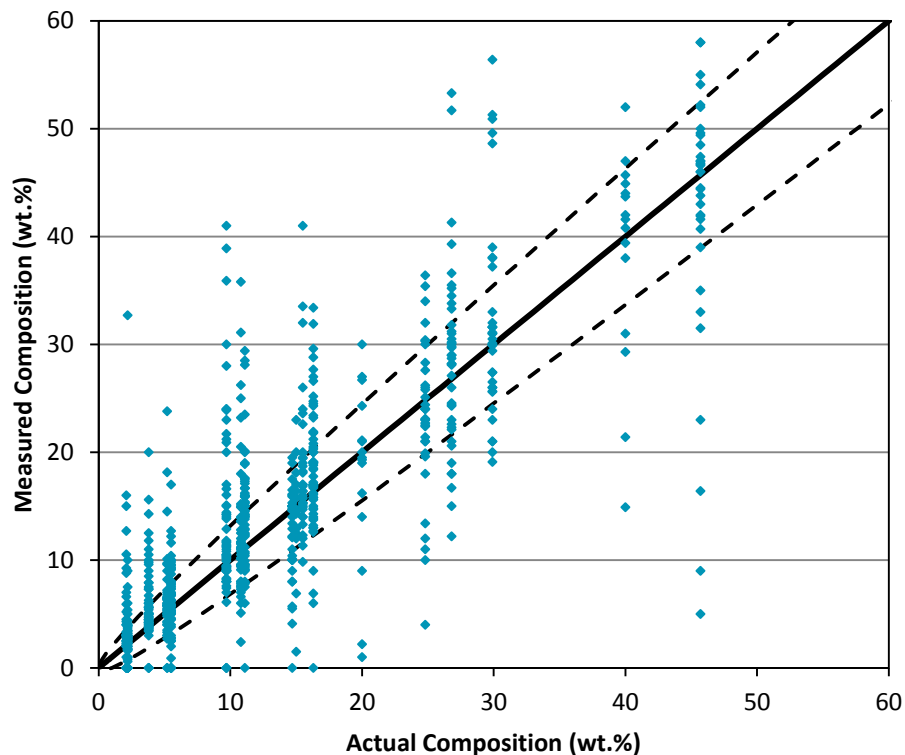
■ ±3%



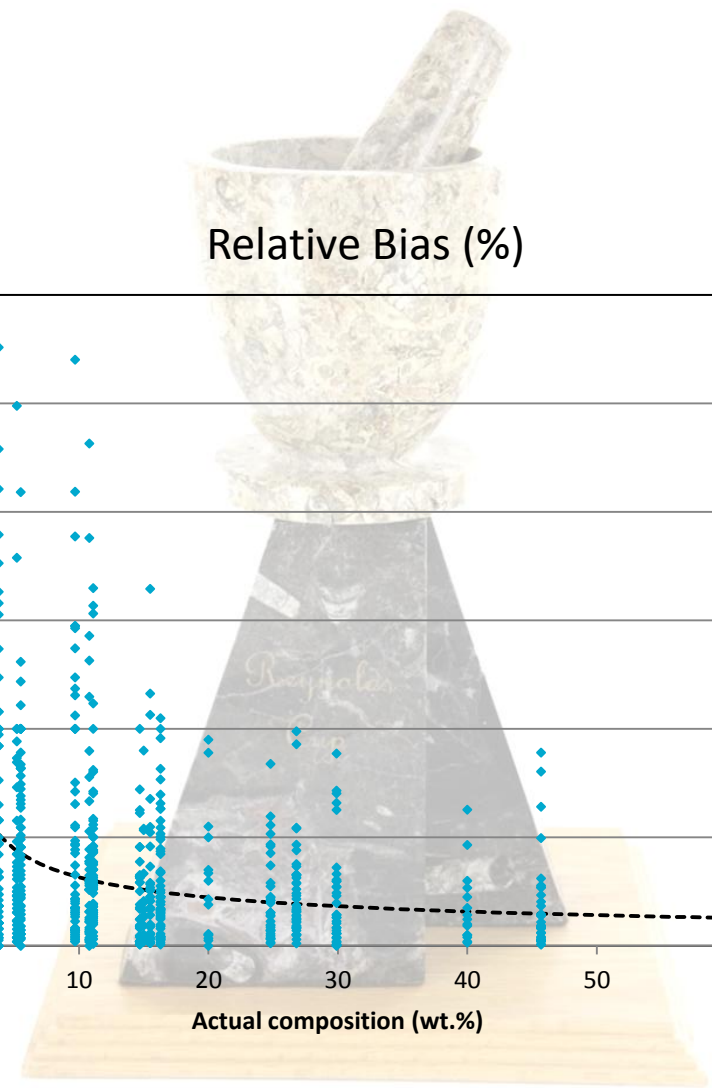
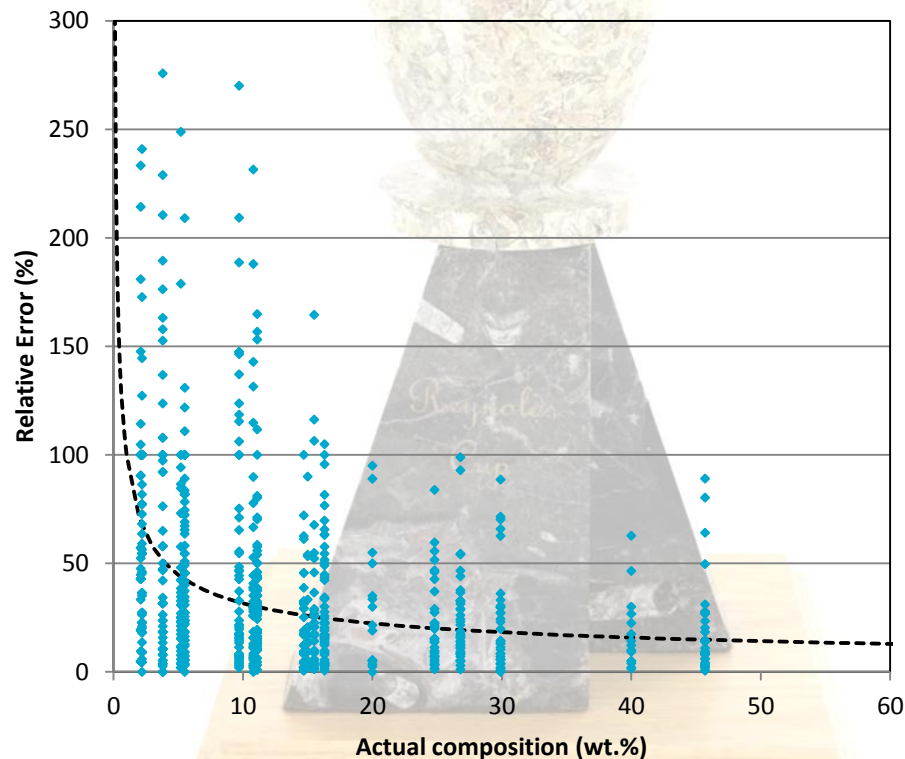
# Quartz – $X^{-0.5}$

Analyses that meet the criteria: 439 (58.3%)

Absolute Bias (wt.%)



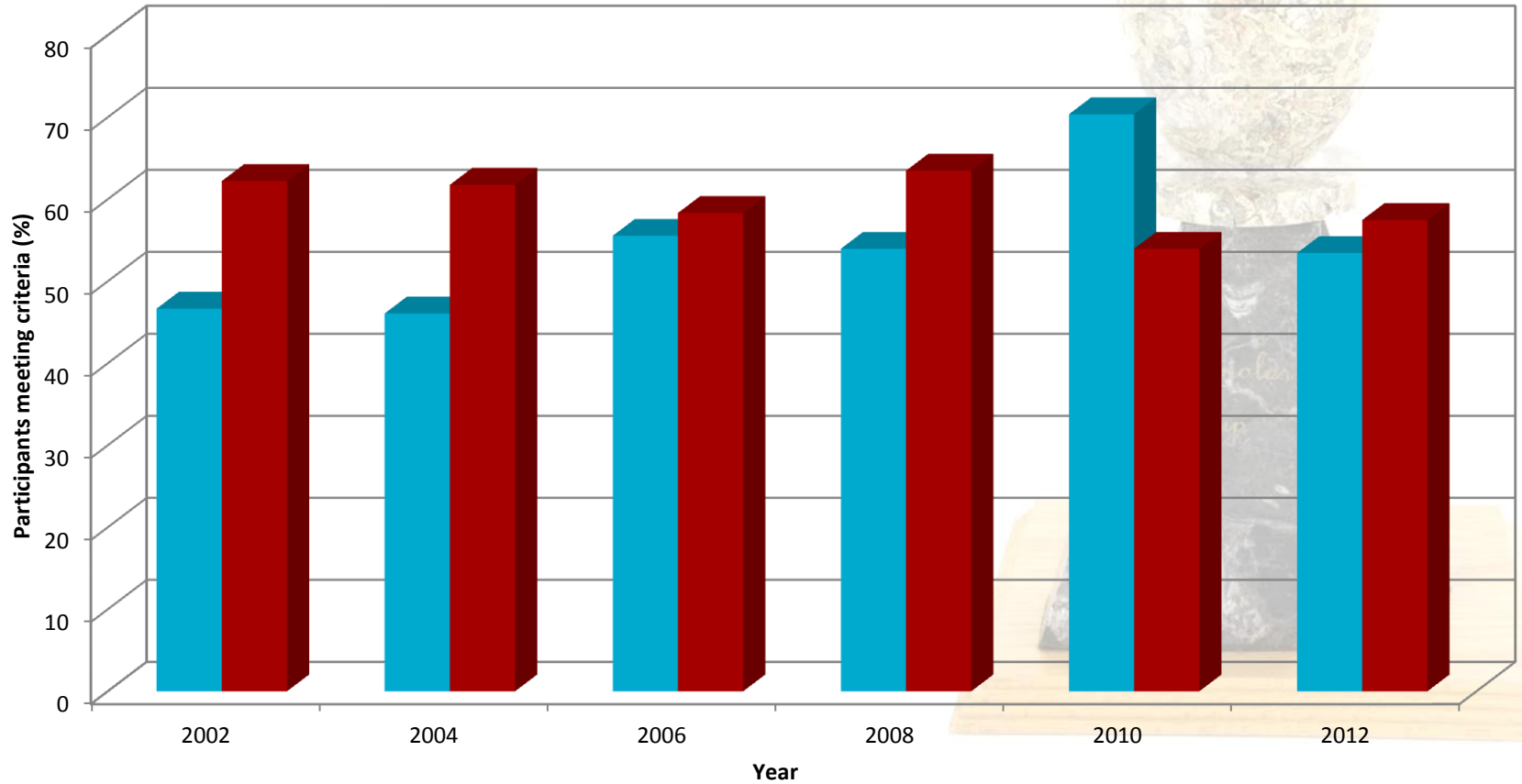
Relative Bias (%)



# Are we there yet?

## Quartz

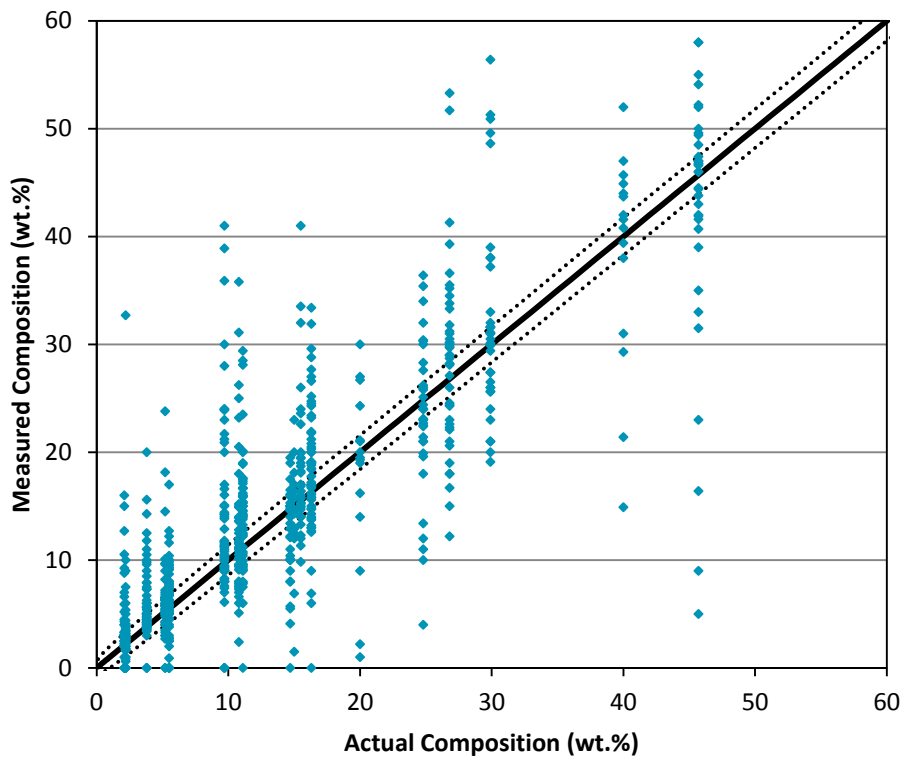
■  $\pm 3\%$  ■  $X^{-0.5}$



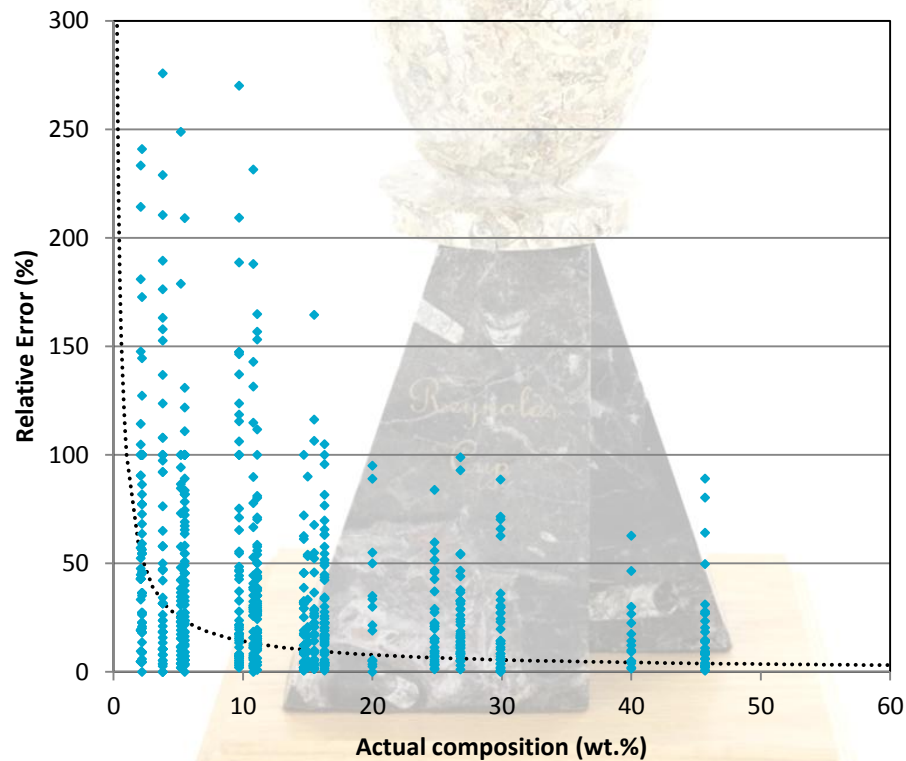
# Quartz – $X^{-0.85}$

Analyses that meet the criteria: 253 (33.6%)

Absolute Bias (wt.%)



Relative Bias (%)

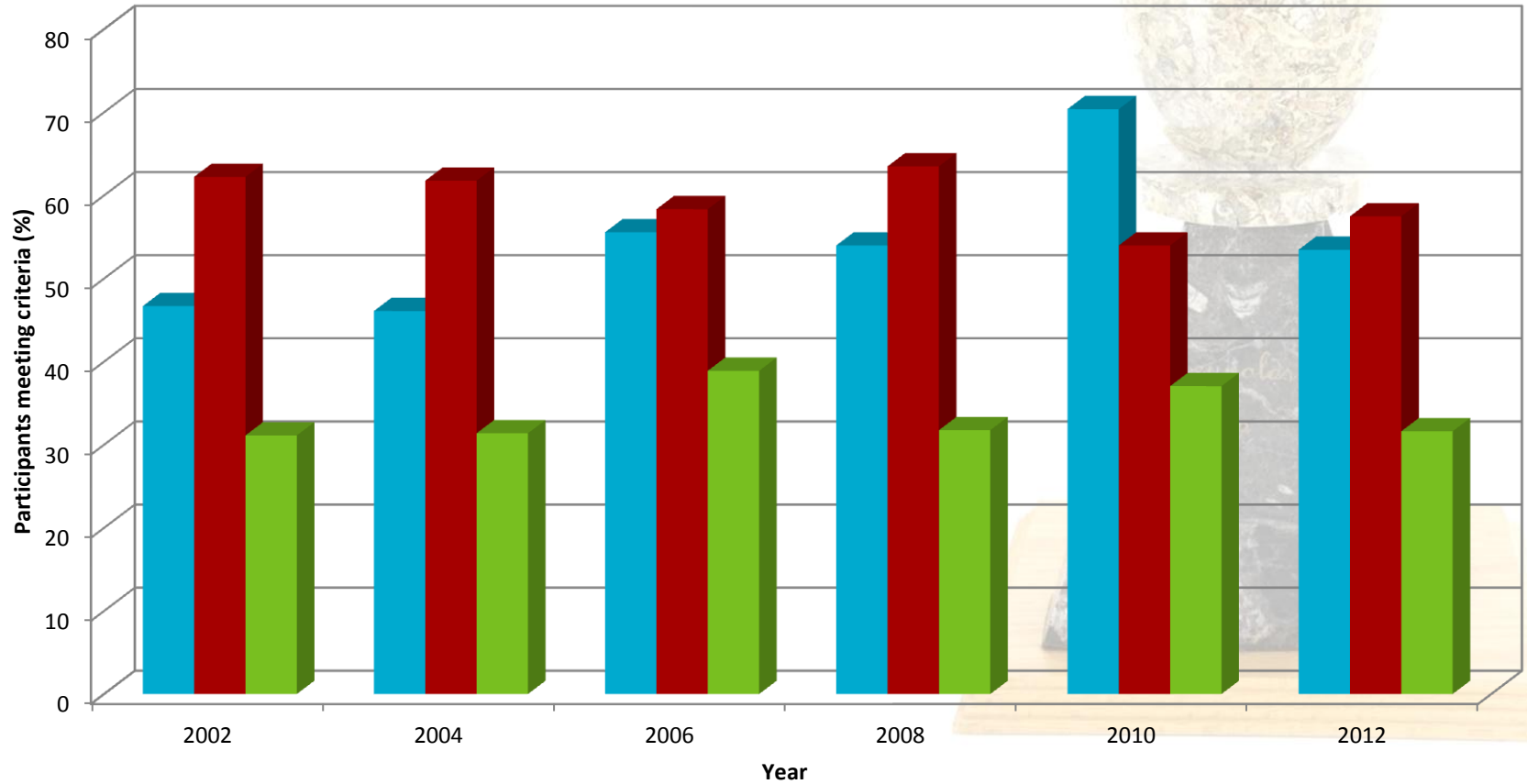


S. Hillier 2003. Quantitative analysis of clay and other minerals in sandstones by XRPD. *Int.Assoc.Sedimentol.Spec.Publ.* 34, 213-251

# Are we there yet?

## Quartz

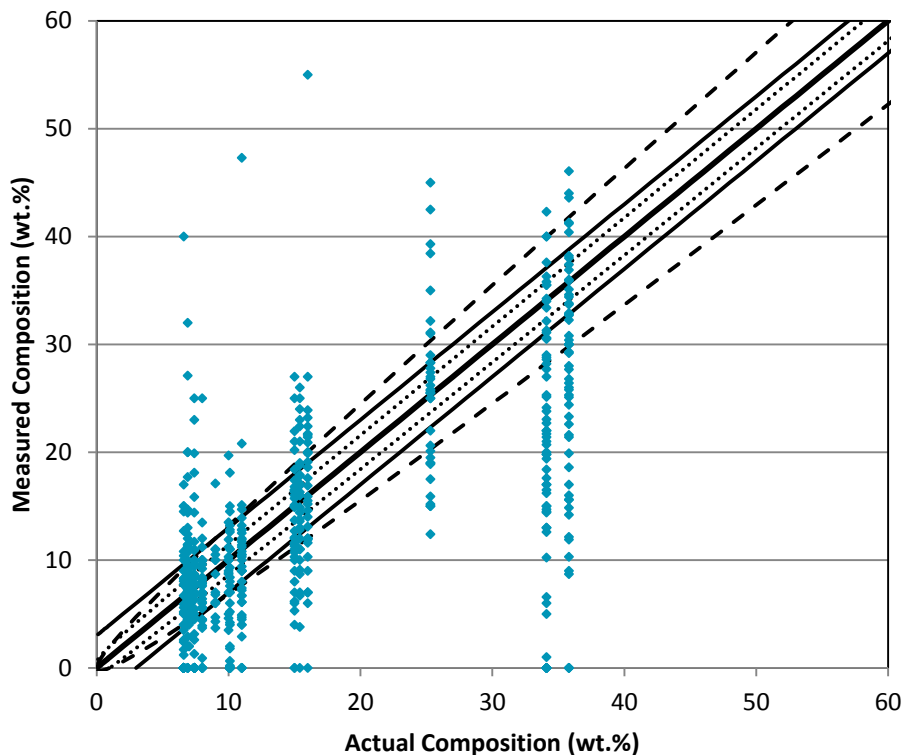
■  $\pm 3\%$  ■  $X^{-0.5}$  ■  $X^{-0.85}$



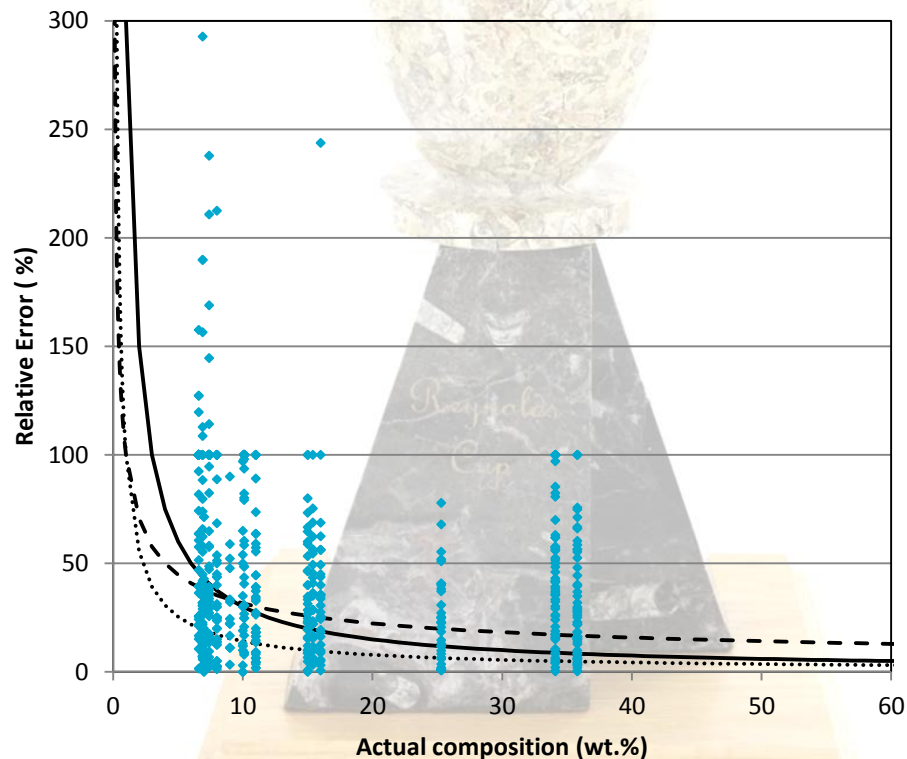
# Kaolin clays – $\pm 3\%$ , $\chi^{-0.5}$ , $\chi^{-0.85}$

Analyses that meet the criteria: 231 (37.8%), 262 (42.9%), 119 (19.5%)

Absolute Bias (wt.%)



Relative Bias (%)

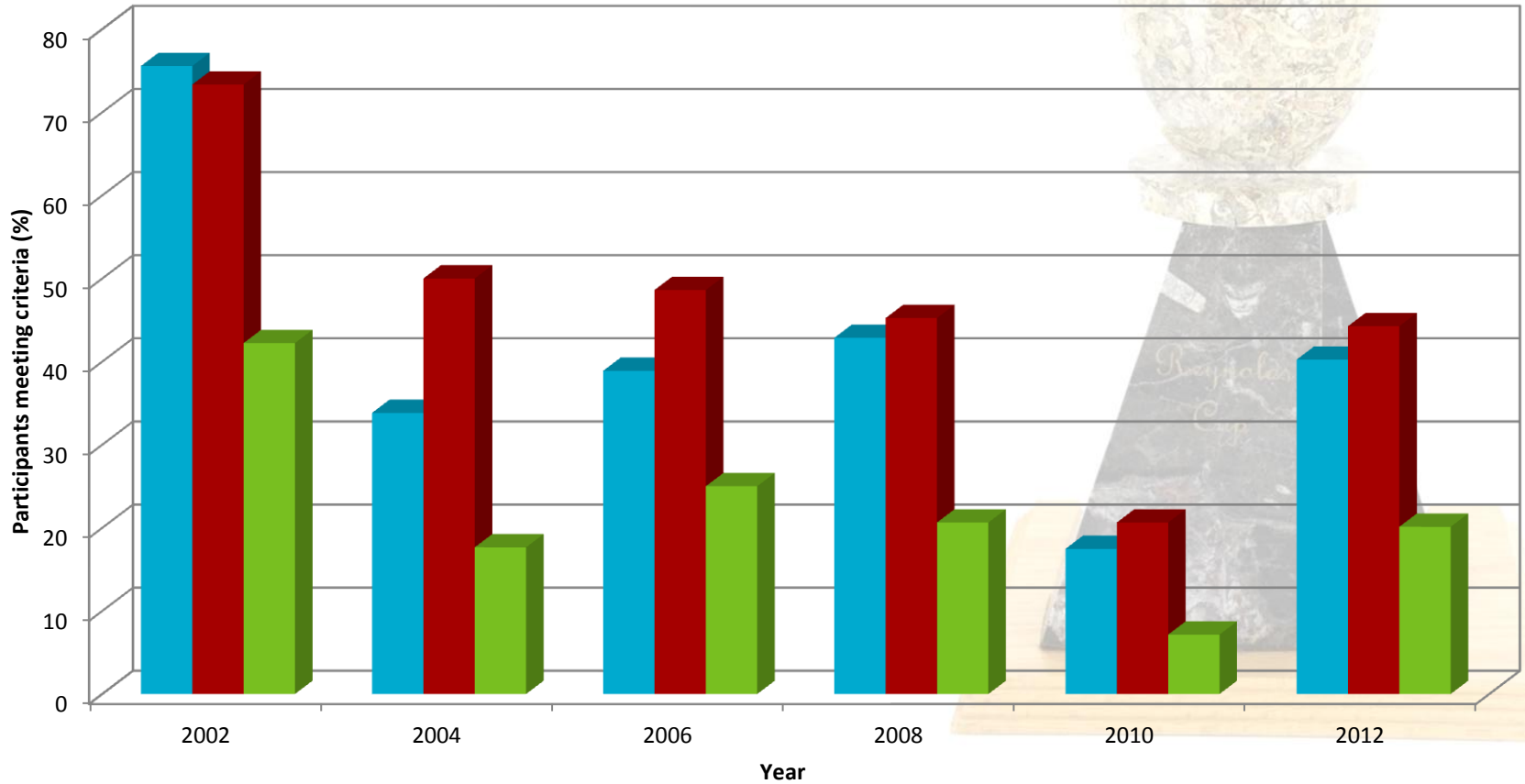




# Are we there yet?

## Kaolin Clays

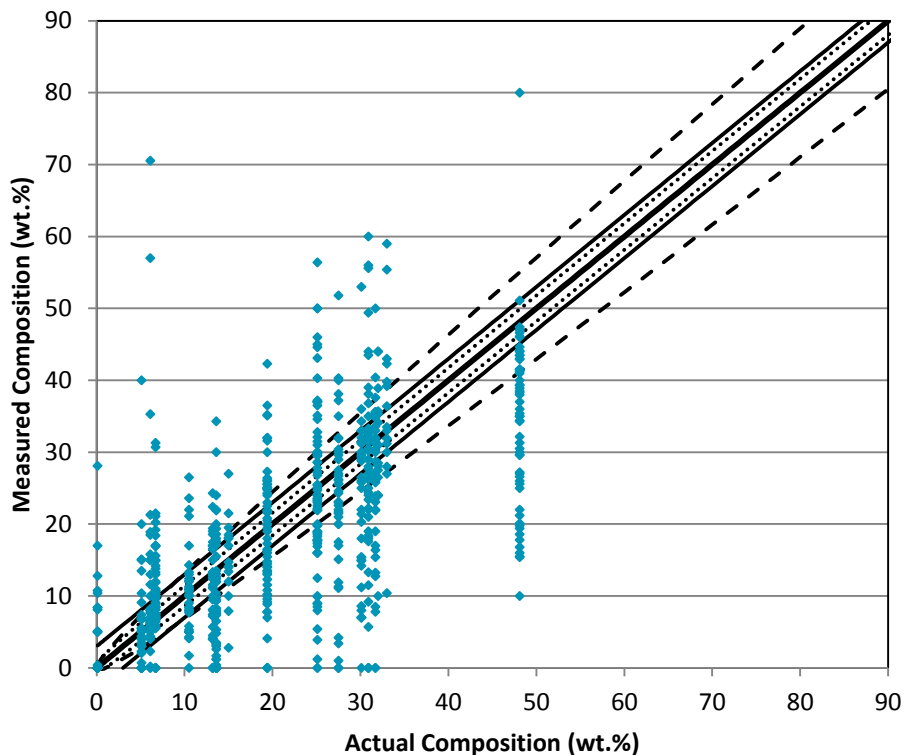
■  $\pm 3\%$  ■  $X^{-0.5}$  ■  $X^{-0.85}$



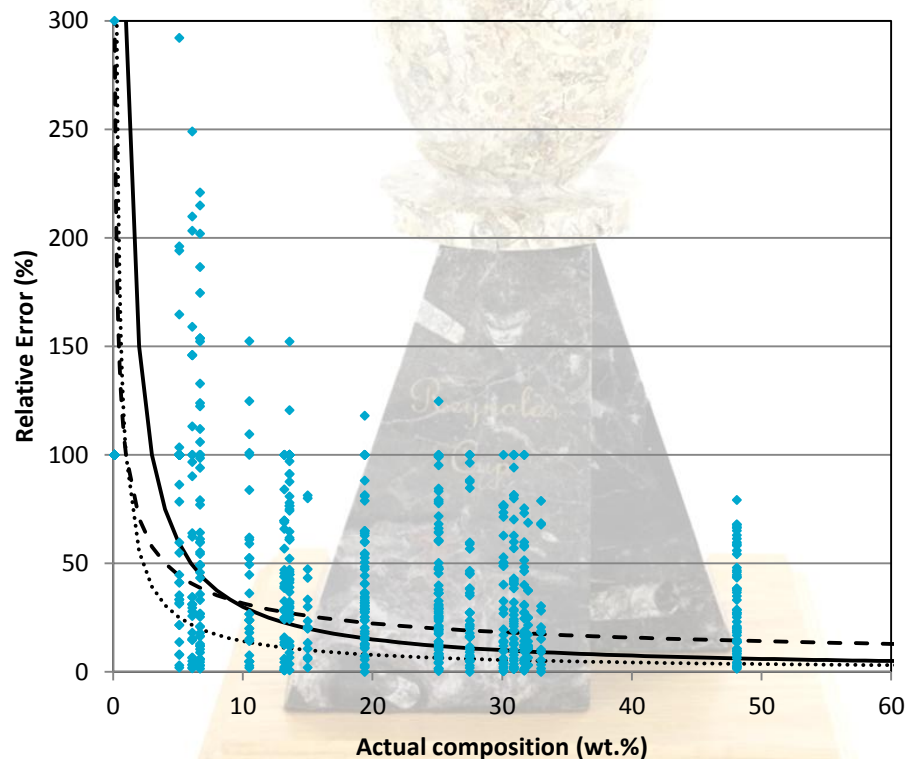
# 2:1 Dioctahedral clays – $\pm 3\%$ , $\chi^{-0.5}$ , $\chi^{-0.85}$

Analyses that meet the criteria: 241 (32.4%), 300 (40.3%), 157 (21.1%)

Absolute Bias (wt.%)

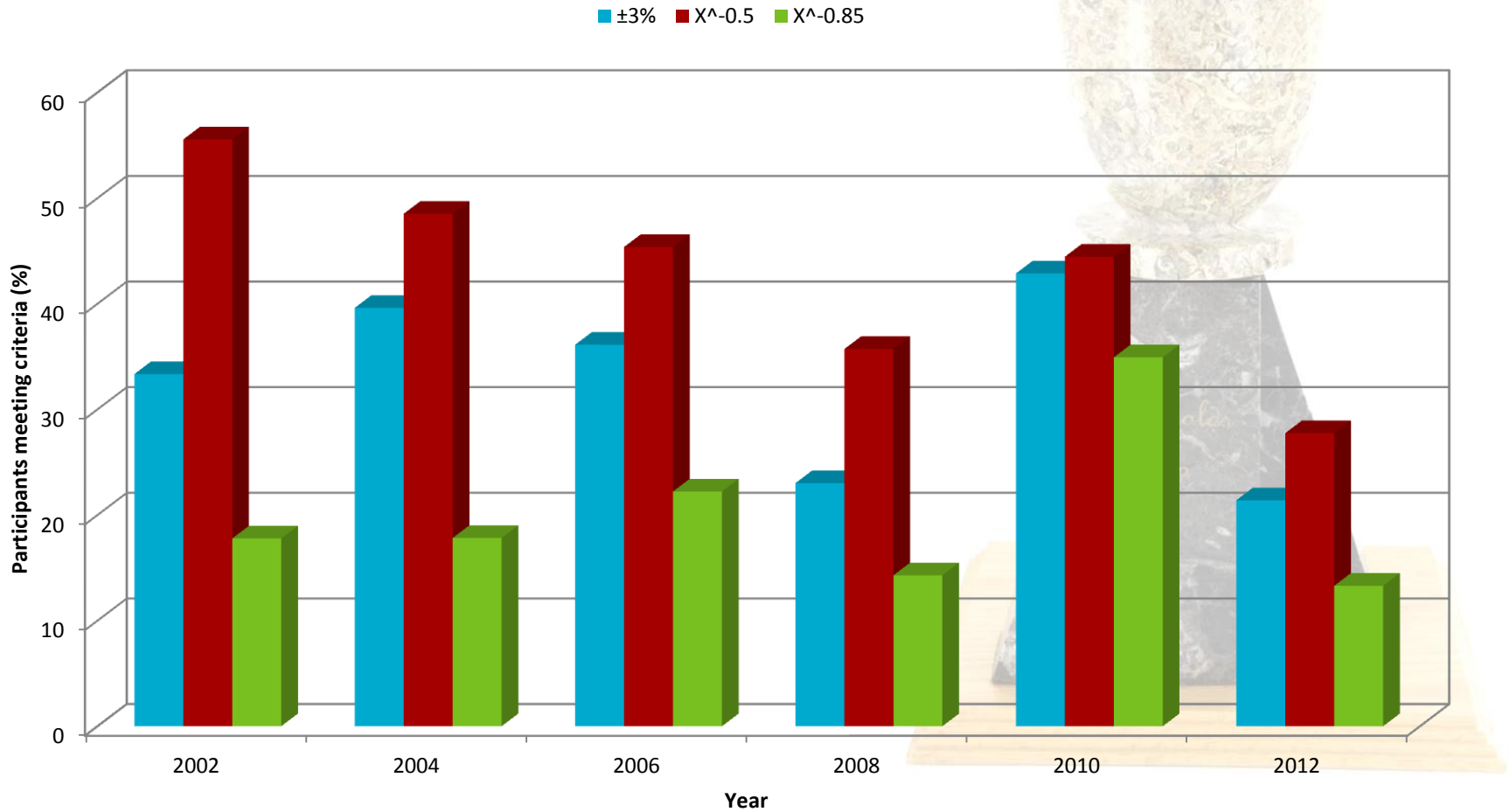


Relative Bias (%)



# Are we there yet?

## 2:1 Dioctahedral Clays



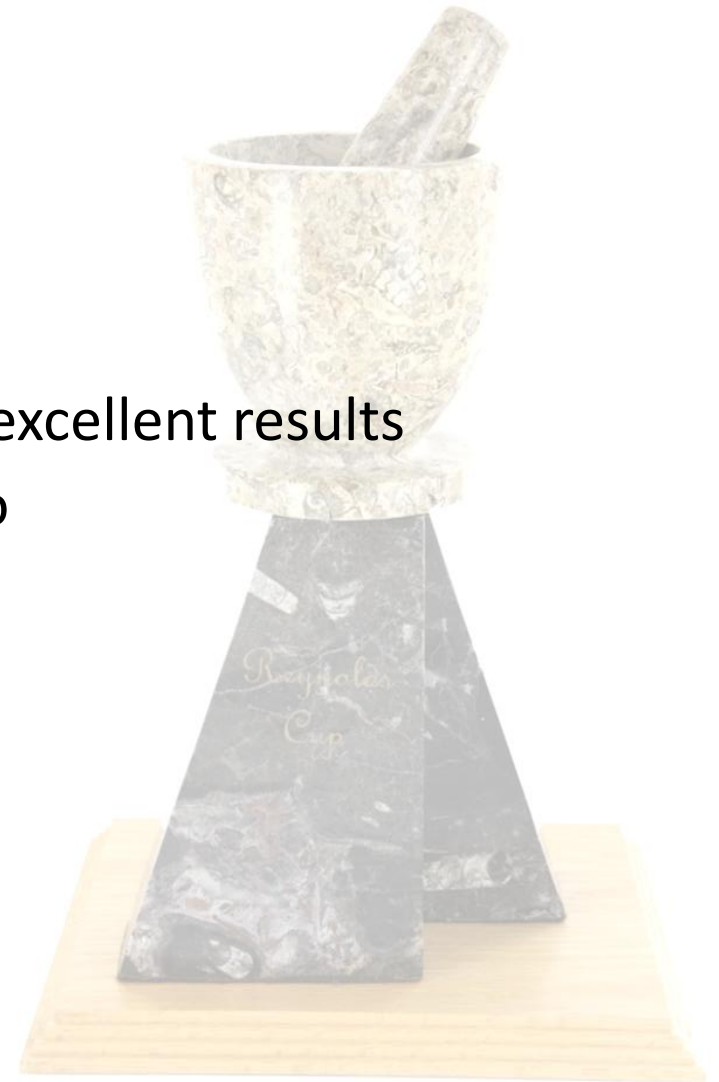
# Summary

- 10 years of Reynolds Cup round robins
- 6 contests
- 18 sample mixtures
- 35 non-clays and 8 clay mineral groups
- 367 participants
- Almost 10,000 analyses
- 6 winners from 6 different countries



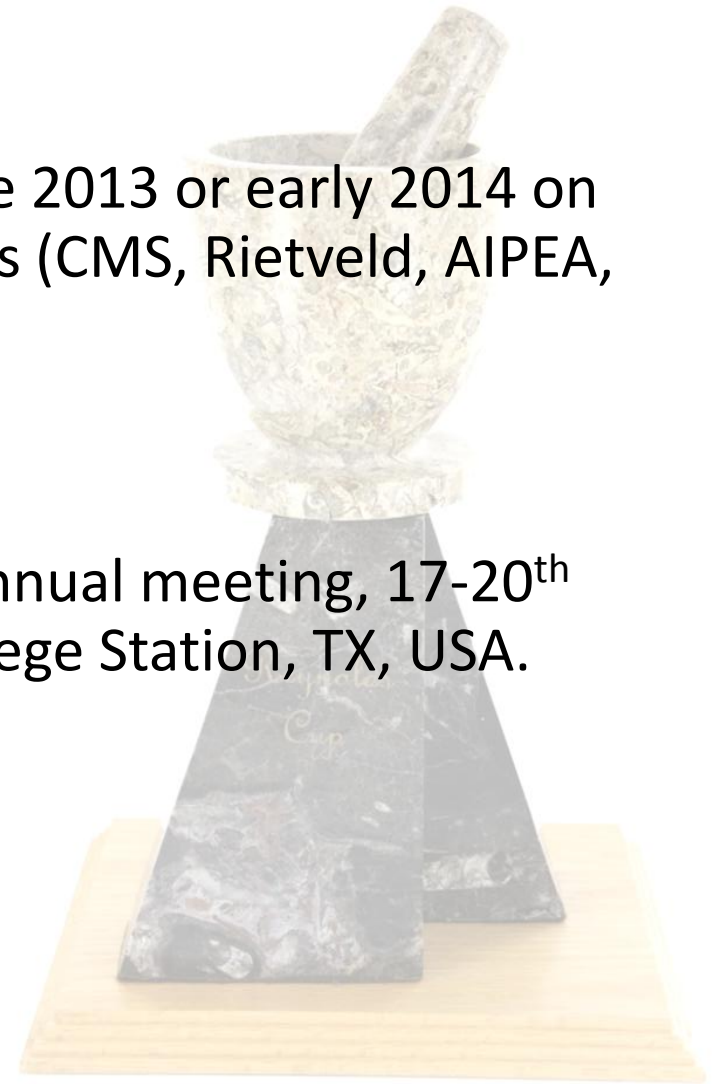
# Conclusions

- Has accuracy improved?
  - As individuals
  - As a group
- Some participants consistently achieve excellent results
- Some participants have a long way to go
  - Sample preparation
  - Instrument settings
  - Inappropriate or incorrect use of Software



# Reynolds Cup 2014

- Announcement of 7<sup>th</sup> round robin in late 2013 or early 2014 on the CMS web site, and various email lists (CMS, Rietveld, AIPEA, etc)
- Winners announced at the 2014 CMS annual meeting, 17-20<sup>th</sup> May 2014 at Texas A&M University, College Station, TX, USA.
- GOOD LUCK!



# Thank you

**Land and Water**  
Mark D Raven

**t** +61 8 8303 8497  
**e** [Mark.Raven@csiro.au](mailto:Mark.Raven@csiro.au)  
**w** [www.csiro.au/](http://www.csiro.au/)

**Land and Water**  
Peter G Self

**t** +61 8 8273 8103  
**e** [Peter.Self@csiro.au](mailto:Peter.Self@csiro.au)  
**w** [www.csiro.au/](http://www.csiro.au/)