Problems of quantitative XRD mineral analyses and their solutions by non-Rietveld methods

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Artificial rock composition

Mineral	Mudstone, RC-AR1 (%)	Siltstone, RC-AR2 (%)	Calcareous Mudstone, RC-AR3 (%)
Quartz (821-382, Columbia)	20	40	15
K-Feldspar (821-386, Microcline)	8	10	2
Plagioclase (821-001, Albite)	8	10	2
Calcite (821-383, Iceland Spar)	5	3	17
Dolomite (821-392, Montana)	3	2	5
Halite (821-026, EM Science)	3	2	2
Pyrite (821-394, Mexico)	2	3	2
Siderite (821-237, Antigonish)	3	2	5
Barite (821-353, Drilling)	2	2	2
Gypsum (821-389, Selenite)			5
Total Non-clay	54	74	57
Kaolinite (821-307, Kaofine90)	9	7	10
2:1 AI clay (821-384, RM30, <2.0µm)	25	9	28
2:1 Fe clay (821-118, Nontronite #33)	7	6	5
Fe-chlorite (821-216, CCa2)	5	4	
Total clay	46	26	43
Total	100	100	100

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Reynolds Cup 2002



Cumulative Error (differences from actual)





Problems of quantitative XRD

- Sample representative for the rock
- Homogenous sample
- Internal standard
- Grinding and mixing for quantitative XRD
- Orientation
- Sample density
- XRD pattern recording
- Non-Rietveld quantitative analysis of XRD patterns

Sample representative for the rock

 Statistic methods of sampling in order to make the mineralogical sample representative for the investigated geological object (techniques widely used for the evaluation of mineral deposits)

Homogenous sample

- How to make small samples needed for different analyses representative for a bulk piece of solid rock?
- Coarse grinding to pass ca. 0.4 mm sieve
- Splitting



Internal standard

- Absent from the investigated samples
- Isometric sub-micron grains (no need for grinding, no orientation)
- Possibly small number of reflections and minimum coincidences
- Possibly big scattering power (strong reflections=less standard needed=less dilution of the sample)
- 20% Al₂O₃ widely used (RIR)
- 10% ZnO selected by Środoń et al. (CCM, 2001)

Grinding and mixing for quantitative XRD

- Wet-grinding to avoid amorphisation
- Non-water grinding to avoid destroying clay aggregates
- Limited time to avoid peak broadening related to crystalsize reduction
- Normal distribution instead of lognormal to avoid "tail" of coarse grains
- Enough sample to minimize contamination by the mill material
- Solution: 5 min grinding of 3g sample in 4 ml methanol or hexane in McCrone mill. Mixing with ZnO by the same technique. Drying on magnetic stirrer to avoid segregation.
- Longer grinding of some pure standards

Particle Size Distribution, McCrone and Tema Mills (O'Connor & Chang, 1986)



Grinding - special cases

- Pyrite will oxidize soon: ground samples cannot be preserved for longer times
- Gypsum may dehydrate partially to bassanite
- If dissolution-recrystallization possible (halite, gypsum etc.) better to use hexane

Orientation

- Problem of platy particles (layer silicates, gypsum, feldspars) present in the sample as individual grains
- Very strong effect on relative intensities
- Partial remedy: screening+side-loading
- Perfect remedy: spray-drying







Sample density

- Sample density controls the depth of penetration of X rays, i.e. the degree of departure from ideal focussing geometry
- Result: sample density affects peak shape and position
- Partial remedy: standardize sample prep. as much as possible

Reproducibility of XRD pattern

RC-AR1a-pe/ Reynolds Cup Artificial Rock 1a/ 3g-hex-5min/ 1



- C-AR1a-pe/Reynolds Cup Artificial Rock 1a/ 3g-hex-5min/1 - File: RC-AR1a-pe.RAW - Type: 2Th/Th locked - Start: 5.000 ° - End: 65.000 ° - Step: 0.020 ° - Step time: 10. s - Temp Operations: Import

RC-AR1b-pe/ Reynolds Cup Artificial Rock 1b/3g-hex-5min/1 - File: RC-AR1b-pe.RAW - Type: 2Th/Th locked - Start: 5.000 ° - End: 65.000 ° - Step: 0.020 ° - Step time: 10. s - Temp
Operations: Y Scale Mul 1.062 | Y Scale Mul 0.917 | Import

Reproducibility of XRD pattern

RC-AR2a-pe/ Reynolds Cup Artificial Rock 2a/ 3g-hex-5min/ 1



- Control Revealed Control Revealed Rev

RC-AR2b-pe/Reynolds Cup Artificial Rock 2b/3g-hex-5min/1 - File: RC-AR2b-pe.RAW - Type: 2Th/Th locked - Start: 5.000 ° - End: 65.000 ° - Step: 0.020 ° - Step time: 10. s - Temp
Operations: Import



Reproducibility Test: 5 splits from same shale sample



Spray-dried clay: photo of S. Hillier



Spray-dried clay: photo of S. Hillier



Spray-dried clay: photo of S. Hillier



Spray-dried vs. side-loaded artificial rock



Spray-dried vs. side-loaded albite



XRD pattern recording

- 2Θ range which includes diagnostic peaks for all mineral components
- Sufficiently fine recording step to reproduce peak profiles well
- Sufficient recording time to assure high intensities and small counting error
- Maximum slits assuring pure quartz 3.34A peak intensity within the linear range of the counter
- Possibly high peak/background ratio
- Our solution: 2-65°2Θ, step 0.02°/2min (105 min/sample), THERMO X'TRA with solid-state detector, slits: 0.9/1.6/1.6/0.3 receiving

Quantitative analysis of the XRD pattern: theory1

Wt.% of mineral X (%X) in a mixture m is proportional to the intensity of a reflection of mineral X (I_x)

Standard:
$$\% X = \frac{I_x \mu_m^*}{K_x}$$
 Spike: $\% S = \frac{I_S \mu_m^*}{K_S}$

 μ_m^* = mass absorption coefficient of the mixture K_x = constant for a chosen reflection of mineral X I_x = intensity of a chosen reflection of mineral X %S = Wt.% of an internal standard (spike)

$$\text{MIF} = \frac{K_X}{K_S} = \frac{I_X \cdot \% S}{I_S \cdot \% X}$$

 MIF_{X} (=RIR_X) does not depend on: Recording conditions, μ_{m}^{*} of mixture, or the type and content of other phases in the mixture

Quantitative analysis of the XRD pattern: theory2

Therefore:

$$\% X = \frac{(I_X \cdot M_S \cdot 100)}{(I_S \cdot \text{MIF} \cdot M)}$$

- *M_s* = mass of internal standard (spike)
- *M* = mass of investigated sample
- I_X = intensity of mineral X reflection used in MIF
- $I_{\rm S}$ = intensity of internal standard (spike) reflection used in MIF

%X = percent of mineral X in mass M (in investigated sample)

Non-Rietveld quantitative analysis of the XRD pattern: practice

- Recording standards and measuring MIFs
- Precise mineral identification
- Selections of standards appropriate for the identified minerals
- Measurement of peak intensities used by MIFs
- Calculation of mineral composition of the sample
- Verification of the result