

Rietveld analysis/whole pattern fitting method for quantification of clay components

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Abstract:

This study explores the use of Rietveld refinement and whole pattern fitting as an alternative technique for quantitative clay analysis. Rietveld refinement uses known atomic structure to model the phase components present. This allows the refinement of atomic parameters through least squares analysis until the calculated pattern generated by the model agrees with the experimental pattern. Rietveld analysis can yield accurate and reproducible quantitative results. Other traditional X-ray diffraction methods are highly subject to variations in diffracted peak intensity due to preferred orientation. This is not a limitation in the Rietveld method.

Introduction:

Although important to industry, current quantification methods of expandable clay components, such as Montmorillonite, are not standardized techniques, and many different calculations exist. Most of these methods require X-ray diffraction data from clays collected at ambient conditions, another set of data after the crystalline lattice is expanded by glycolization, and a third set of data after heating to collapse the lattice. Comparisons of the three data sets and calculations using the diffracted peak intensities, although a traditional method, are highly subject to variations (including preparation techniques).

Quantitative analysis is also achieved with a structure refinement technique called Rietveld refinement. This method uses known atomic structures to generate a model of all the phase components present, then allows for refinement of the atomic parameters with least squares analysis until the model agrees with the experimental pattern. Rietveld analysis can also yield accurate and reproducible quantitative results; as well as compensate for inaccurate peak intensity due to preferred orientation.

Known atomic structures are available for most of the basic clay types, which means the quantification of clays under ambient conditions is possible with Rietveld, at least for the non-expandable clay components. However, very few of the expandable clay lattices have been characterized. The expanded clay lattices are unstable due to the cation exchange properties and absorption of water. This makes the clays difficult to crystallize in a form suitable for X-ray structure determination. Therefore, good atomic structure data for Montmorillonite is not readily available.

This method explores the effectiveness of using Rietveld analysis with the current atomic structure models for quantification of mixed layer or expandable clays by X-ray diffraction data.

Experimental:

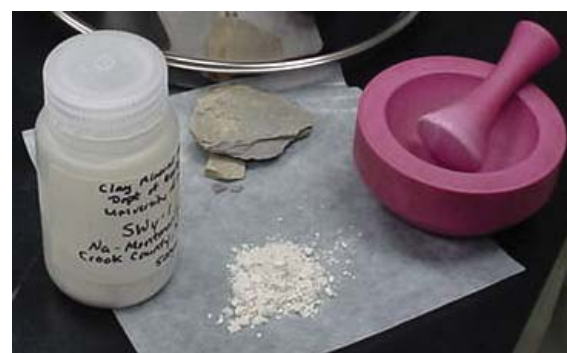


Figure 1. Fithian Illite standard from Wards, and Wyoming Na-Montmorillonite (smectite) were used for this study

1. Sample preparation:

Illite standard (from Wards) was ground and sieved to - 400 mesh (~ 37 microns). Na-Montmorillonite Standard SWy-1 (from Clay Mineral Society, Dept. Of Geology, University of Missouri, Crook County, Wyoming).

Mixtures of the solid samples at various concentrations were combined to a total weight of 0.4 grams and mixed by hand for 30 minutes each with a wire whisk. The entire aliquot was packed in a 0.5 mm deep, round aluminum sample holder and placed in the Rigaku MiniFlex II™ benchtop X-ray diffractometer. The following dilutions were made.

Montmorillonite/Illite

- 1:2 dilution - 0.2000 g "mont"/0.2000 g "illite"
- 1:4 dilution - 0.1000 g "mont"/0.3000 g "illite"
- 1:6 dilution - 0.0664 g "mont"/0.3336 g "illite"
- 1:10 dilution - 0.0400 g "mont"/0.3600 g "illite"
- 4:1 dilution - 0.3000 g "mont"/0.1000 g "illite"

2. Data collection parameters:



Figure 2. The MiniFlex II, a portable X-ray diffraction system with standard copper radiation source, was used for this study

Instrument configuration and scan parameters

Instrument: MiniFlex II benchtop diffractometer
 Radiation: Cu K α power setting 30 kV 15 mA
 Wavelength: 1.54059 Å
 Slits: DS: Variable coupled to θ axis RS: 0.3 mm
 Detector: Scintillation counter NAI (TI)
 Optic: Graphite monochromator for removal of K β and fluorescence
 Scan range: 2° to 64° 2 θ
 Scan type: $\theta/2\theta$ coupled
 Step size: 0.03°
 Scan speed: 2 sec. dwell time per step; total scan time 1 hour

Data:

XRD plots and composition of "pure standards"

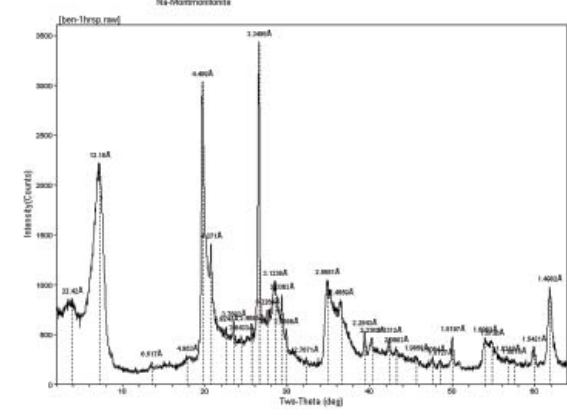


Figure 3. XRD plot of "pure" Montmorillonite

An accurate crystal structure for Montmorillonite has not been derived experimentally, because it has not been possible to prepare a single crystal of this mineral. Most of the XRD Montmorillonite patterns publicly available are either experimental d-spacing and intensity lists or calculated patterns. Following are two examples:

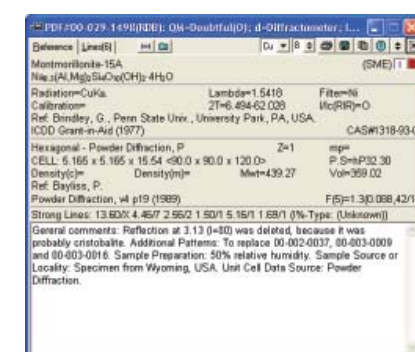


Figure 4. A hexagonal reference pattern from ICDD (International Centre for Diffraction Data), Newton Square, Pennsylvania; Ref. Brindley, G., Penn State University

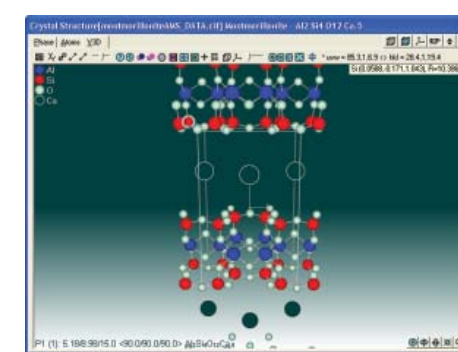


Figure 5. Atomic structure pattern from American Mineralogist, 87 (2002) p. 966-975, Ref.: Gualtieri, A. F. Crystal symmetry: Triclinic: P1, a = 5.18 Å, b = 8.98 Å, c = 15.0 Å, α = 89.9342, β = 89.991, γ = 90.0364

Crystal symmetry listed in this pattern is hexagonal-packed (Figure 4). Lattice parameters are a = 5.165, c = 15.54. In *An Introduction to the Rock Forming Minerals*, Deer, Howe and Zussman refer to the Si $_2$ O $_5$ layer of smectites (Montmorillonite) as a pseudo-hexagonal network but the overall symmetry is monoclinic [1]. This pattern may only be reflecting part of that symmetry.

Crystal symmetry of this Montmorillonite is triclinic (Figure 5 and 6). Most Montmorillonite unit cells are monoclinic with a space group of C2/m [1].

Ruizite atomic structure is a better match than the triclinic pattern. It is monoclinic C2/m and yields a better Rietveld refinement (Figure 7). However, it is still not the correct atomic structure pattern or chemical composition for Montmorillonite.

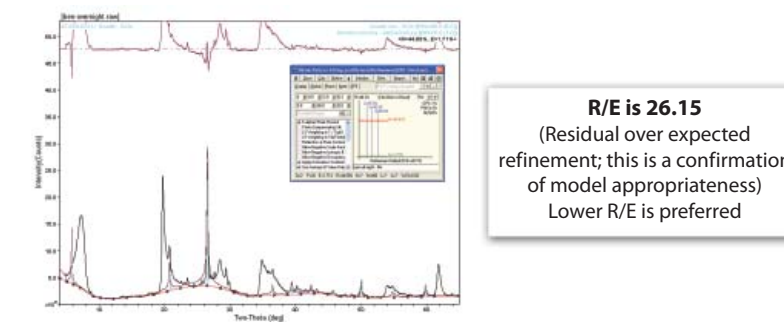


Figure 6. Lattice for the triclinic Montmorillonite is not a good match and yields a poor refinement (Note the high R/E value)

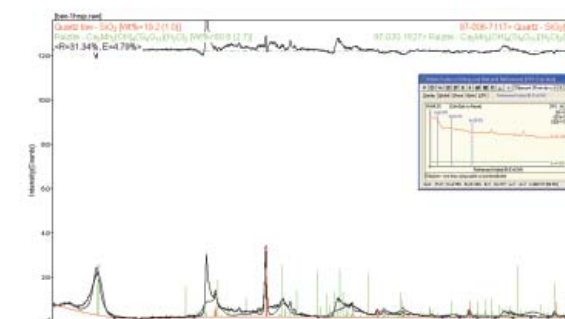


Figure 7. Rietveld refinement for Montmorillonite sample using a mineral called Ruizite (Note the lower R/E value)

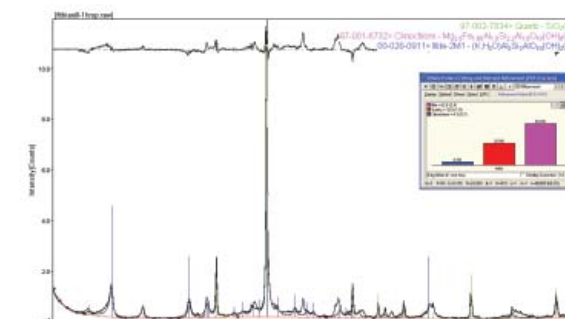


Figure 8. Rietveld refinement for illite sample (Note the lower R/E value)

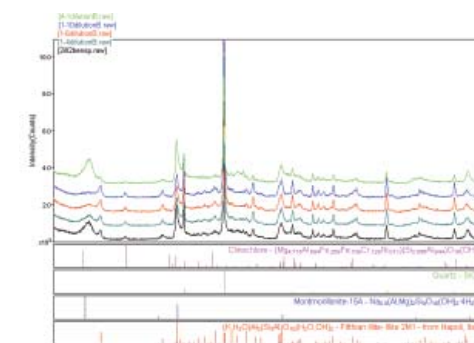


Figure 9. Raw data XRD patterns for dilution series of Montmorillonite and illite

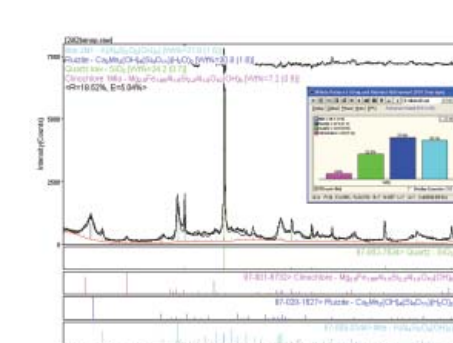


Figure 10. Rietveld refinement results for 1:2 dilution of Montmorillonite. A low R/E residual indicator is desired for a good refinement (i.e. 3.68)

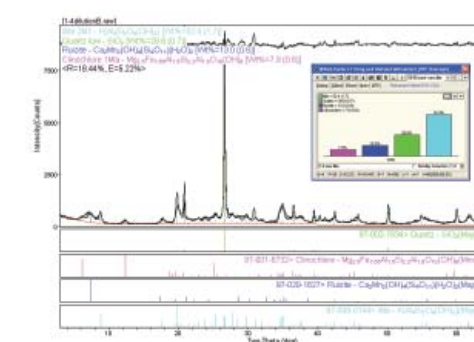


Figure 11. Rietveld refinement results for 1:4 dilution of Montmorillonite. A low R/E residual indicator is desired for a good refinement (i.e. 3.53)

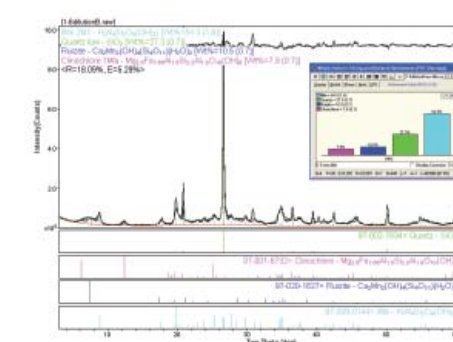


Figure 12. Rietveld refinement results for 1:6 dilution of Montmorillonite. A low R/E residual indicator is desired for a good refinement (i.e. 3.42)

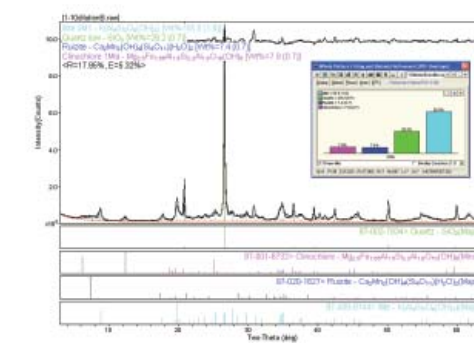


Figure 13. Rietveld refinement results for 1:10 dilution of Montmorillonite. A low R/E residual indicator is desired for a good refinement (i.e. 3.37)

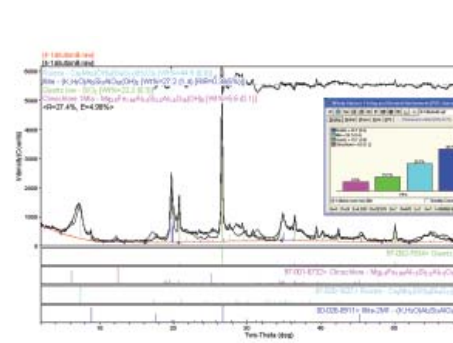


Figure 14. Rietveld refinement results for 4:1 dilution of Montmorillonite. A low R/E residual indicator is desired for a good refinement (i.e. 3.53). The R/E indicator is showing a higher residual area that has not been incorporated into the atomic model.

Table 1. Rietveld results with Monoclinic C2/m model

| Dilutions | Montmorillonite Theoretical weight % Rietveld weight % | Illite 97-009-0144 Theoretical weight % Rietveld weight % |
|--|--|---|
| Concentration of actual Montmorillonite in "pure" sample | *80.8% | *0% |
| Concentration of actual illite in "pure" sample | *0.0% | *63 |
| 1:2 dilutions 0.2 g "mont"/0.2 g "illite" | 40.4 | 31.5 |
| | 30.8% | 37.8% |
| 1:4 dilutions 0.1 g "mont"/0.3 g "illite" | 20.2 | 47.3 |
| | 13.0% | 52.4% |
| 1:6 dilutions 0.0664 g "mont"/0.3336 g "illite" | 13.5 | 52.5 |
| | 10.5% | 54.3% |
| 1:10 dilutions 0.04 g "mont"/0.36 g "illite" | 8.08 | 56.7 |
| | 7.4% | 55.5% |
| 4:1 dilutions 0.3 g "mont"/0.1 g "illite" | 60.6 | 15.75 |
| | 45.7% | 29.7% |

*Pure clay standards are difficult to find. Commercially available clay standards usually contain other compounds.

Conclusions:

Even with a less-than-perfect Montmorillonite model (Figure 6), dilutions were fairly accurate at low-to-mid Montmorillonite concentrations. With a better model, the weight % accuracy should improve. The imperfect model loses effectiveness at the higher concentrations of Montmorillonite and overestimates the concentration of illite. Area in the diffraction pattern that should be assigned to Montmorillonite is erroneously assigned to illite due to missing reflections in the smectite model.

However these results are encouraging and indicate that Rietveld method can be applied for quantification of smectites in an altered clay environment, when an appropriate model is incorporated.

Future work:

Future work in this area would include using current atomic modeling programs to translate the triclinic Montmorillonite atomic structure pattern to more closely simulate theoretical C2/m monoclinic symmetry for a typical sodium-rich Montmorillonite.

Once an appropriate model is achieved, it would be prudent to obtain different samples of Montmorillonite and other smectites to further test the application of this Rietveld method.

References:

- [1] Deer, W.A., Howe, R.A., and Zussman, J., *An Introduction to the Rock Forming Minerals*, Longman House Publishing, thirteenth edition 1982 pp 264-269.

All XRD patterns were collected with the Rigaku MiniFlex II benchtop diffractometer. The MiniFlex II is a portable X-ray diffraction system with a compact size (~ 24" W x 14" D x 26" H), capable of both low angle and high angle bulk materials analysis. A graphite monochromator is available for samples where fluorescence is possible.

All XRD data analyzed with Jade, a product of Materials Data Incorporated (MDI), 1224 Concannon Blvd., Livermore, California 94550; telephone: 925-449-1084; FAX: 925-373-1659; mdi@materialsdata.com

All XRD reference patterns were from two databases:

1. PDF 4-2007 from ICDD, Newton Square, PA
2. Release 2007-2 from FIZ/NIST Inorganic Crystal Structure Database (ICSD), Standard Reference Data Program, National Institute of Standards and Technology, Gaithersburg, MD

Acknowledgements:

I would like to thank Janine Shipman with New Park Drilling Fluids Lab, Katy, Texas and Robert Uresti with Baker Hughes, Houston, Texas for sample contributions and suggestions.