Instructions in Using GSAS Rietveld Software for Quantitative X-ray Diffraction Analysis of Portland Clinker and Cement

Paul Stutzman
Leslie Struble

NIST
National Institute of
Standards and Technology
U.S. Department of Commerce

Instructions in Using GSAS Rietveld Software for Quantitative X-ray Diffraction Analysis of Portland Clinker and Cement

Paul Stutzman

Materials and Structural Systems Division
Engineering Laboratory

Leslie Struble

University of Illinois
Civil Engineering

June 1, 2015

U.S. Department of Commerce
Penny Pritzker, Secretary

National Institute of Standards and Technology
Willie May, Under Secretary of Commerce for Standards and Technology and Director

Table of Contents

List of Figures

List of Tables

Abstract

X-ray powder diffraction analysis is used in the cement industry as a direct analytical method for phase identification and quantitative analysis of clinker and cements. Quantitative methods initially relied on the development of calibration curves, employing multiple reference mixtures of cement phases with an internal standard to develop a plot of diffraction peak intensity ratios vs. mass fraction ratios. Obstacles to this approach were the availability of reference standards that adequately replicated those phases in the clinker or cement, and the ability to accurately measure diffraction peak intensities because of severe peak overlap. The Rietveld method for analysis of powder diffraction data addresses both of these difficulties through use of refineable crystal structure models to calculate the individual phase diffraction patterns and a whole-pattern fitting procedure to minimize the difference between the measured diffraction pattern and set of calculated phase patterns. This approach has revolutionized the application of X-ray powder diffraction in many scientific disciplines, including that of hydraulic cements, but can be a complicated method to learn. This tutorial is intended to provide an introduction to the application of Rietveld analysis to portland cement clinker and cements using examples developed from one of the NIST SRM clinkers and two portland cements.

Introduction

This document is an instructional guide in the use of Rietveld software for quantitative phase analysis of portland cement and related materials using powder X-ray diffraction (XRD). It presumes that the user is familiar with portland cement composition and with XRD analysis and has a basic understanding of crystallography and of Rietveld analysis. It provides step-by-step instructions with associated XRD data in the use of Rietveld software for quantitative phase analysis of portland cement.

Rietveld in this context refers to a technique for characterizing crystalline materials by refining neutron or X-ray diffraction patterns. A theoretical pattern is computed based on the crystal structure parameters of all phases in the material, parameters used to model peak shape for each phase, and instrument parameters (specimen height offset, for example). This theoretical pattern is refined until it best fits the measured pattern, using a least squares approach. As noted by Young [1], this approach might better be called a "whole-pattern-fitting structure refinement", but the name Rietveld is simpler and acknowledges the importance of Rietveld's work in the development of the technique. Additional information may be found in Young [2] and Lutterotti [3], among others. Young [1] gives an overview of the technique that briefly explains its underlying

mathematics and the various refinable parameters. The technique may be used to refine the crystal structure parameters in a single phase or simple mixture, or to determine the mass fraction of each phase in a complex mixture. The latter is the focus of these instructions.

There are several programs available for Rietveld refinement. The program known as Generalized Structure Analysis System (**GSAS**)[1,2] was selected for these instructions because it is well documented, it is in the public domain, and it is regularly updated. Once the user becomes familiar with **GSAS** (with the help of these instructions), it should be a relatively straightforward task to apply these procedures to any other codes. **GSAS** was written by Larson and Von Dreele and the appropriate reference to use is [4]. The accompanying graphical user interface, **EXPGUI**, was written by Toby [5].

The Rietveld refinement requires detailed crystal structure information for all phases in the sample. The parameters include the space group and unit cell parameters and the position in the unit cell of all atoms in the phase. If any phase is not included in the refinement, the mass fraction results are biased even for the phases included. For this reason, use of the technique must be preceded by careful *qualitative* phase analysis.

These instructions make use of crystal structure parameters for phases in portland cement and related materials that were compiled previously from various publications. The user of these instructions will undoubtedly accumulate new parameters as additional structures are published or refined.

This document is similar to instructions prepared by Cranswick and Swainson [6] but is more focused and specific to cement materials. You may wish to refer to those more general instructions when getting started with **GSAS**. You may also wish to refer to the manual included with the **GSAS** download [4], but it is rather out of date and does not describe the graphical user interface that is used here, so the instructions of Cranswick and Swainson [6] are probably more useful. The related program **CMPR** [7] can also be used for displaying diffraction data (including **GSAS** experiment file), converting XRD patterns from one format to another, manual- and auto-indexing, peak fitting and other tasks. No instructions are given here for this program.

These instructions are self-contained, in so far as they do not require the user to generate diffraction patterns. The instructions include links to measured XRD patterns and instrument parameters.

---

[1] Certain commercial equipment, instruments, or materials (including suppliers and software) are identified to enhance understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

[2] GSAS, EXPGUI, and CMPR are available from:
http://www.aps.anl.gov/Xray_Science_Division/Powder_Diffraction_Crystallography/

Rietveld Refinement

In the Rietveld refinement method as described by Young [1], the powder pattern is calculated according to the following equation:

$$y_{ci} = S \sum_K L_K |F_K|^2 \varphi(2\theta_i - 2\theta_K) P_K A + y_{bi}$$

(1)

where

> y_{ci} is calculated intensity at point i
> K represents index (hkl) of Bragg reflections contributing to intensity at point i
> S is phase scale factor
> L_K contains Lorentz, polarization, and multiplicity factors
> F_K is structure factor for Bragg reflection
> φ is profile function (diffractometer effect)
> P_K is preferred orientation
> A is absorption
> y_{bi} is background at point i.

Then the calculated pattern is refined to optimize the fit to the measured pattern according to the following equation:

$$Q = \sum_i w_i (y_{oi} - 2y_{ci})^2$$

(2)

where

> Q is residual difference
> y_{oi} is observed intensity at point i
> y_{ci} is calculated intensity at point i
> w_i is a weighting factor, $1/y_{oi}$ [1].

Several criteria for the refinement are recognized. In these instructions we are using chi squared (X^2). This and other criteria are discussed by Toby [8]. X^2 has a value never less than unity and is defined in the following equation:

$$\chi^2 = {Q}/{N}$$

(2)

where

> Q is residual difference, as above, using the standard deviation weighting factor
> N is the number of data points (or the degrees of freedom, a related parameter).

Tasks

A number of individual tasks comprise these instructions. Single-phase tasks were designed to provide familiarity with the technique and users are encouraged to perform at least one of these single-phase tasks.

More complicated tasks involving clinker and cement utilize the KOH-sugar (KOH-S) extraction residue and the salicylic acid-methanol (SAM) extraction residues to refine parameters prior to refining the bulk material. These selective chemical extractions concentrate specific phase groups, simplifying the diffraction pattern and concentrating the residue phases, thereby enhancing their detection limits. Such chemical extractions are not required in analysis of cementitious mixtures but are generally and highly recommended. It is possible to do refinements on a single pattern of clinker or cement, but the results are not likely to be satisfactory. If you are planning to use the method on repeated samples of a material such as portland cement, which contains a complex set of phases with the same crystal structure parameters, it is a good strategy to use patterns for KOH-S, SAM, and perhaps nitric acid extraction residues to refine the crystal structure parameters more accurately for phases in each residue, and then to use the resulting parameters in your subsequent analyses.

In a subsequent section on steps in the refinement, more detailed instructions are given for these tasks. And in a subsequent section on assessment, expected results are described.

Peak profile parameters are required for fitting. These parameters describe the instrument contribution to the diffraction peak shape. **GSAS** includes a file inst_xry.prm that can be used as an example in establishing a file specific to your instrument.

For fitting an XRD pattern, the peak profile parameters should be established using data collected using the same instrument that was used to collect the pattern. Such data should be collected on a sample with negligible strain and relatively large crystallite size, such as National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 660, LaB_6. However, the peaks from this sample are much sharper than seen with portland cement phases, so more steps are required to refine the peak shape parameters. An alternative is to use a single-phase material with a peak shape more like that of the cement phases. This could be one of the NIST SRM diffraction intensity standards or a fine-grained quartz powder.

The sequence of operations in a Rietveld refinement is, to some extent, discretionary and depends on the objective of the refinement. However, results may be affected by the refinement sequence and a poor sequence may cause the program to crash. The sequence given here is based in part on Table 1.5 of Young [1], in part on Cranswick and Swainson [7], and in part on the personal experience of the authors.

Perform the following tasks. More detailed instructions are provided in the section titled Steps in Refinement. If you have any trouble, you may wish to check the section titled Helpful Hints.

1. Download the Rietveld software **GSAS** and its graphical user interface **EXGUI** plus related files from https://subversion.xray.aps.anl.gov/trac/EXPGUI . Versions are available for various types of personal computers, and you should use the most recent version for your specific computer. Note: the installation program does not set up a link to **GSAS** in the Windows startup menu, so if you desire such a link, you must set it up yourself.

2. Download and save the Cements_Data.zip file from the WEB-based tutorial at (http://concrete.nist.gov/~bullard/) that contains the following five data sets:

A) Cement crystal structures in multiple data formats: Individual GSAS experiment files (.EXP), a standardized crystallographic information file (.CIF) that is readable by most Rietveld codes, and a table (.TBL) format, which is the simplest to read for manual data input. In addition, collections of individual phases by group (alite, belite, aluminate …) are provided in GSAS .EXP form. These data should be considered read-only to retain the original values. A key is provided within the data folder to explain the data files (Appendix A).

B) An instrument parameter file (.PRM) and one or more of the single phase patterns provided (corundum, periclase, lime, or quartz). Using these files and the crystal structure parameters from the structure archive (TBL folder) for the phase you selected, refine the single-phase pattern to generate a new peak profile parameters file. Save this file to use in subsequent refinements. The single phase patterns and the subsequent XRD patterns were collected using the same instrument (at NIST) and so are suitable for these tasks, though not for use in refinement of patterns collected using your own instrument.

C) Next, work with the XRD patterns for one of the complex mixtures (SRM 2686 clinker, proficiency cement A, or proficiency cement B). Perform a qualitative analysis of the pattern using **CMPR** or some other software. Use the crystal structure parameters for all the identified phases from the structure archive and your instrument parameters file to refine the mixture to determine the amount of each phase. Compare results to published values (see section titled Assessment).

D) Finally, work with the XRD patterns for the extraction residues of the same complex mixture you analyzed in Task 4, both SAM (SRM 2686 clinker, proficiency cement A, or proficiency cement B) and KOH-S (SRM 2686 clinker, proficiency cement A, or proficiency cement B).

Perform a qualitative analysis of each pattern as above. Using the crystal structure parameters for all the identified phases from the structure archive and your

instrument parameters file, refine the extraction residues of the same complex mixture to determine refinements for the crystal structure parameters. Then use these new parameters to refine the mixture to determine the amount of each phase. The XRD file header for the SAM extraction residue contains the insoluble residue mass percent value, allowing for a recalculation of the residue phases on a whole-clinker basis.

Compare results to published values (see section titled Assessment). Compare results of Tasks 4 and 5 (the computed mass fraction of each phase and the figure of merit for the clinker/cement without using extraction residues and with using extraction residues).

Files

GSAS produces or uses a large number of files. All are stored in the folder in which you read or created the exp file. The more important files when using **GSAS** are described here. Most of this information is derived from the **GSAS** manual [4].

1. Experiment file—This is the main data and control file and has the extension .exp. It includes the input and output of the refinement. A new file is generated for each refinement. That is, when the experiment file is opened by one of the routines in **GSAS** that is able to modify its contents, a new version is usually produced, and the next routine in **GSAS** to access the experiment file opens this new version. Earlier .exp files are then renamed as .On, where n is a number that increases incrementally.

2. Powder or histogram file—This is the raw data for the refinement and has the extension .gsas. Routines such as **CMPR** are available to convert common XRD file formats (such as .gsa, .raw, or .fxye) into .gsas files.

3. Instrument parameter file—This is the set of instrument-dependent peak profile parameters and has the extension .prm. It is possible to begin with generic parameters and then refine them using powder data for material with a well-defined crystal structure.

4. List or line printer output file—This is the output of the refinement and has the extension .lst. This file is updated during each refinement cycle. It includes the figure of merit (X^2), the computed mass fraction of each phase, and the density of each phase. It is recommended that you view this output throughout the refinement process. You can open and view this using the Lstview tab in Expgui. The Lstview tab also provides a file trim option (file, trim *.lst) to retain only the most recent portions of the file, which will otherwise get quite long as a refinement proceeds.

Steps in Refinement

This section is taken largely from Cranswick and Swainson [6]. Additional information is given there, with many figures showing the interface window and many specific examples. The program offers many options, but the instructions here are limited to those you are expected to use in these tasks.

1. Run **EXPGUI**. This opens a text window and an interface window. Use the interface window to set refinement parameters. Some results will be returned to you in the text window, which can also be used to monitor the lst file. The interface window has drop-down menus at the top that lead to buttons that call for specific action and tabs that take you from one window to another. From here on, instructions are given only for this window (in terms of menu, button, or tab).

2. Open a new or existing .exp file. When you first run EXPGUI, the program instructs you to open an existing file. If **EXPGUI** is already running, you may open a file using the file drop-down menu. If you wish to create a new file, type in the desired name and click the **read** button.

3. Enter crystal structure data for phases in the .exp file. Note that qualitative analysis must be done, using **JADE** or other XRD pattern display code before undertaking the refinement. (Note that the **GSAS** program refines rhombohedral structures in the hexagonal setting.) To enter structure data, select the **phase** tab and then the **add phase** button. This will bring up an **add new phase** dialog where you input the phase title, the Space Group (R −3 c) (make sure to include the spaces), and the unit cell values. Then select the **add** button. **GSAS** will then give a symmetry analysis output for you to check to make sure you have entered the space group correctly (use the International Tables or similar database to validate the output). Select **continue** once you are satisfied with the structure data. This will give the main **EXPGUI** screen with the cell information but no atoms.

Now select the **add new atoms** button and add in the atom information using the keyboard.

Select the **add atoms** button to go back to the main **EXPGUI** screen where all the crystallographic information is now visible. The **GSAS** default values for vibrational parameters, UISO (0.025), are usually too large for inorganic structures, so it is better to reset the starting UISO values to 0.01 (by selecting the UISO values one at a time with the mouse and changing to 0.01). The structure database contains vibrational parameters, which are generally best retained and not refined.

An alternate way to add phase data is to import it directly from the database. When you select the **add phase** button and a new box appears, use the option in the lower right to import the phase data. Four options for import file format are provided--select the **GSAS** .exp format (the .cif format is also provided in the database), which will open a third box to search subdirectories for the appropriate .exp file for the phase you wish to load. After selecting a specific .exp file, the **add new phase** box will be automatically filled out with the data for that phase. If the .exp file contains multiple phases, a list will be shown for selection of the specific phase. Select **Continue** and a list of symmetry operators appears; upon acceptance of the defaults, a list of atoms, coordinates, occupancies and vibrational parameters is displayed. Select **add atoms** to complete the import of the remaining structure data as a new phase. You may wish to replace the default phase title in **EXPGUI** to the actual phase name, otherwise it reflects the path and filename of the .exp file.

4. Create or open an instrument parameter file. For the tasks in these instructions, open the file provided, which contains the parameters for the powder data used here. But if you wish to create a new file, select from the top menu **Powder, Instedit.**

The instrument parameter file format is discussed in the GSAS manual.

5. Open a histogram (powder diffraction data). Select the **powder** tab followed by the **add histogram** button. Find and add the data file and the instrument parameter file. If you wish to edit this file, select from the top menu **Powder, Instedit.**

6. Fit the background. This is a preliminary fit, which you will refine below. First run **powpref** followed by **genles** using the buttons. Then fit a **GSAS** background function to the data. Now select the **save in EXP file & exit** icon at the bottom right of the screen to save the fitted background profile. When **EXPGUI** prompts that the EXP file has been modified, select **load new**.

7. Fit the profile. In the **profile** tab, set the **profile type** to **3** (Pseudo-Voight with Finger-Cox-Jephcoat peak asymmetry function).

8. Perform refinements. For each refinement, run **genles** using the buttons, preceeded by **powpref** when you have changed specific variables such as peak profile cutoff, or peak profile, sample displacement, or an instrument parameter. **GSAS** generally will warn you if you are attempting to run **genles** after changing a key parameter. Run **liveplot** (and keep this window open) to see the state of the refinement in terms of how well the calculated pattern is fitting the data. The black crosses are the raw data; the red line is the calculated pattern and the blue line below is the difference. The aim is to get the calculated pattern to match the observed pattern so the difference is as close to a flat line as possible. Set the number of cycles to 8 and in the **profile** tab set the **profile cutoff** to 0.001. (Since

you have changed the peak profile cutoff, you will need to run **powpref** before you run **genles**.)

There is no fixed order in which to release parameters when performing a Rietveld refinement. Ideally, all parameters should be refined simultaneously. But when refining complicated mixtures like clinker or cement, some phases and parameters inevitably correlate, and a sequential refinement reduces the likelihood of problems related to the correlations. The instructions here provide suggestions and should not be blindly followed in all cases.

Monitor the difference profile plot to assess your refinement. A valid refinement shows only minor differences between computed and measured patterns.

Monitor the X^2 in the DOS window. If this increases progressively, the refinement is diverging and you should stop, determine which highly-correlated variables may be creating the divergence and deselect refinement of one, or revert to an earlier .exp file (see the section titled Helpful Hints) and then continue. A correlation matrix is included in the .lst file if Print Option #2 of the **LS Controls** tab of **EXPGUI** is selected.

Multiple parameters may be refined at the same time, but you must be careful if the parameters are cross-correlated, as refinement results may be misleading. The correlation matrix indicates parameters that are cross-correlated. For some parameters a constraint makes sense and reduces potential correlations. For example, specimen displacement affects all phases similarly so a constraint in the peak profile parameters for this variable will hold each to the same value (set through the Peak Profile Constraints window).

Refine scale and background.

Refine the shift, unit cell parameters, and peak (GV) width.

Set peak profile cutoff to 0.001 and run **powpref** and then **genles**.

Helpful Hints

The program is unlikely to crash during refinement of a single phase, especially if you follow the instructions given here. But it may crash during analysis of complicated, multiphase mixtures, even if you follow these instructions. If you are unable to proceed with a refinement, it may be that a window has opened for input but is hidden by other windows and the system is waiting for your response, so it is always worth checking for any such window before terminating the task.

Regularly viewing the lst file in the text window is useful for observing progressive changes in chi-square. The direction of the change in chi-square tells you if the refinement is progressing, digressing, or oscillating. The latter indicates some strong correlation issues that need to be constrained or at least monitored.

Viewing the lst file is also useful for checking that the number of variables being refined corresponds to the number set. Sometimes more are being refined because you have inadvertently attempted to refine highly correlated variables.

Finally, the lst file provides values such as density, lattice parameters, mass fractions, and so on.

If it is difficult to get an acceptable background, an alternative approach is to manually select points to use in the background fit. Run **powder, bkgedit** to bring up the background editing screen. Select background points by pointing and clicking with the mouse and using the **add**, **zoom**, and **delete** options. Then fit a GSAS background function to these points, as above.

If you find that you have mucked up the refinement and the parameters have gone to unreasonable values, the best strategy is usually to go to a previous version of the .exp file. In **EXPGUI**, go into **file open** menu and then select **include archived files**; this lists the previous archived files by time and date. Just select a previous EXP file you expect to be all right. If this turns out to be too late or too early an EXP file, just select another one.

For quantitative XRD, it is generally not necessary to define the site occupancy in each phase. One exception to this recommendation is the ferrite phase, where aluminum and iron (and other elements like Mn and Ti) substitute in tetrahedral and octahedral sites [9]. The site occupancy can be refined in the SAM residue, setting the constraint that their sum is unity. While refining site occupancy improves the pattern fit, it generally affects the calculated mass fraction only a small amount. With XRD, it is both impractical and unnecessary to refine the site occupancy for O or H.

With multiple phases, set the shift to the same value for all phases by constraining the shift parameter for all phases. From the **Constraints** tab in **EXPGUI**, select **Profile Constraints** tab on the lower portion of the window, select **Add Constraint** and a new window titled **New Profile Constraint** will appear. Select the profile term for shift (labeled **shft**), select Continue. A new window titled **New Constraint for Terms** will appear with a list of phases at the top. Highlight all the phases, be sure the diffraction histogram is selected and select **Save** to create the constraint. The scale factors of each phase will continue to be refined individually.

Additional crystal structure parameters for minerals are available, for example in [10].

Discussion

It is very easy to get inaccurate quantitative phase analyses using this method even if the fit looks very good and reasonable. Thus validation of results (for example, using chemical composition) is important. For discussion of the accuracy of quantitative phase analysis using this method, see the two International Union of Crystallography (IUCr) Commission reports on round robins [11-12].

Analytical precision and accuracy for cementitious materials are discussed in the ASTM standard [13].

Although only the salicylic acid-methanol and KOH-sugar extraction residues are provided here, HNO_3 extraction may also be performed to isolate C_4AF and can be very helpful in refining its crystal structure.

Assessment

This section provides guidance to help you assess your results before you move on to the next step.

The phase composition of the SRM clinker is included in the certificate [14] provided when the clinker is purchased from NIST. Values from the SRM certificate are listed in Table 1 along with the uncertainties. The phase composition of the proficiency cement samples determined from an ASTM round robin analysis is listed in Table 2.

Students at University of Illinois in CEE501 (a graduate course) performed a laboratory exercise following these instructions and their lab reports formed the basis for the following comments on assessment. They did not, however, analyze either SAM or KOH-S extraction residues of clinker or cement.

Analysis of a single phase with refinement of crystal structure parameters and instrument parameters should produce a very good fit. An example, periclase, is shown in Figure 1. This had a X^2 of 21.8, a fairly high value, though the figure shows a good fit. Another example, corundum, is shown in Figure 2. This had a X^2 of 13.6. One would expect for these samples a somewhat lower X^2, perhaps below 2.0, but the fits shown are satisfactory for this exercise.

Table 1. Phase composition for the SRM clinker [14].

Phase	Mass Fraction (%)
Alite	63.35±1.29
Belite	18.68±1.42
Aluminate	2.46±0.67
Ferrite	10.76±1.44
Periclase	3.40±0.40
Alkali Sulfates	0.87±0.27

Table 2. Phase composition for the proficiency cements [15].

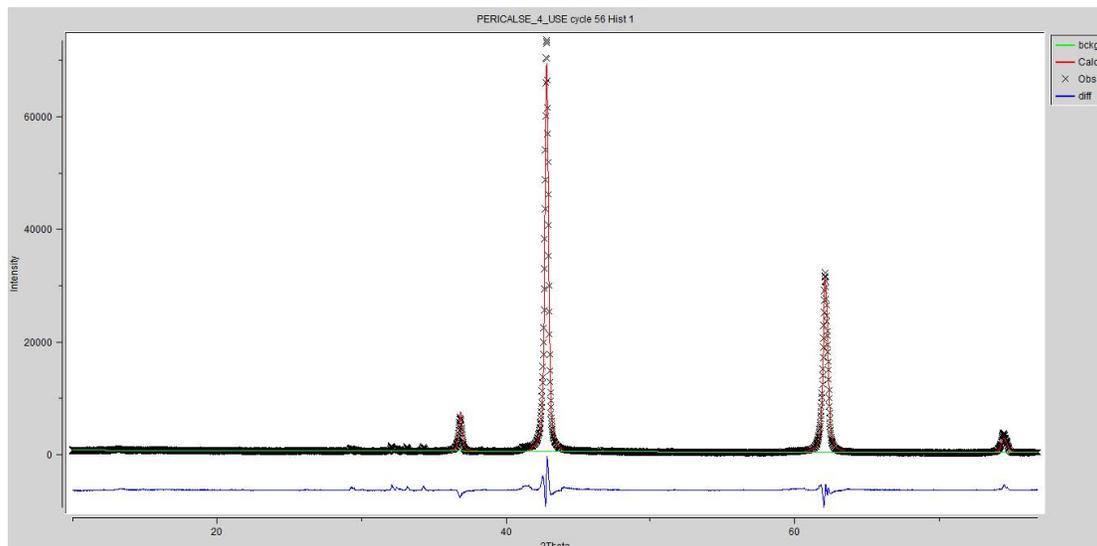| Phase	Cement A	Cement B
	Mass Fraction (%), mean ± standard deviation	
Alite	59.9±2.7	63.5±2.3
Belite	16.8±2.6	12.1±2.2
Aluminate	4.3±1.6	3.5±1.2
Ferrite	9.8±1.7	10.1±1.2
Periclase	1.0±0.3	1.4±0.3
Arcanite	0.7±0.5	0.2±0.2
Aphthitalite	0.0±0.1	0.1±0.1
Anhydrite	1.2±0.8	0.1±0.2
Bassanite	1.8±0.9	0.2±0.3
Gypsum	0.9±1.2	5.1±1.7
Calcite	2.7±1.1	2.5±1.0
Lime	0.1±0.2	0.2±0.3
Portlandite	0.3±0.6	0.7±0.8
Quartz	0.0±0.1	0.0±0.1

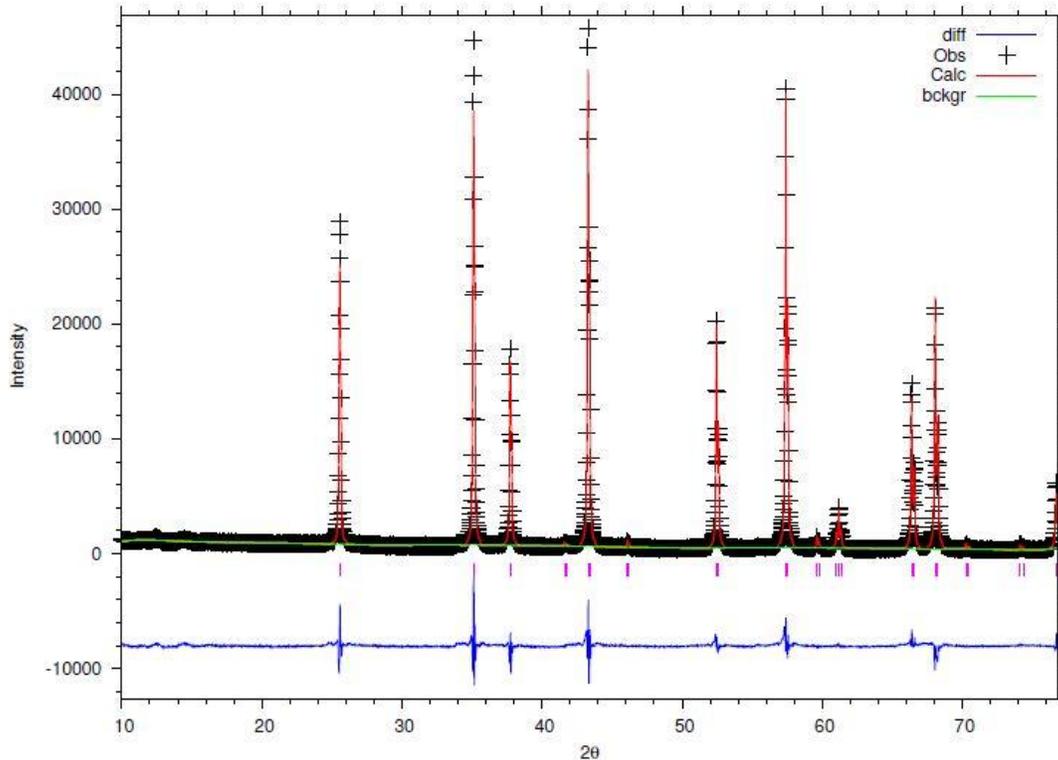**Figure 1. Refinement of the single-phase periclase.**

Figure 2. Refinement of the single-phase corundum.

Analysis of complicated mixtures such as clinker and cement is much more difficult. An example of a poor fit of the SRM clinker is shown in Figure 3 and Table 3. It is evident from the plot and even more evident from the quantitative results that the fit is poor. X^2 was 26.7, high but not that much higher than the fits above. Taylor [9] provides ranges of clinker phases with alite comprising 50 % to 70 %, by mass; belite 15 % to 30 % by mass, aluminate 5 % to 10 %, and ferrite 5 % to 10 %. Periclase may occur up to about 5 % the alkali sulfates may occur up to a few percent, by mass, and the calcium sulfates up to about 5 % by mass. These ranges can vary from the stated values depending upon the clinker or cement, but the ranges provide a sense of what to expect and results that deviate, such as those in Table 3, bear additional attention. Nonetheless, refinement of this pattern should be continued before any conclusions are drawn. Unfortunately, the student experienced problems with the program when attempting further refinements.

A better fit is shown in Figure 4 and Table 4, also of the standard reference clinker. The X^2 was 13.8, still quite high, but a much better fit than in Figure 3. And the phase fractions in Table 4 are much more sensible than those in Table 3. With additional experience, the fitting will be improved, but these results are within the specified range for each phase.
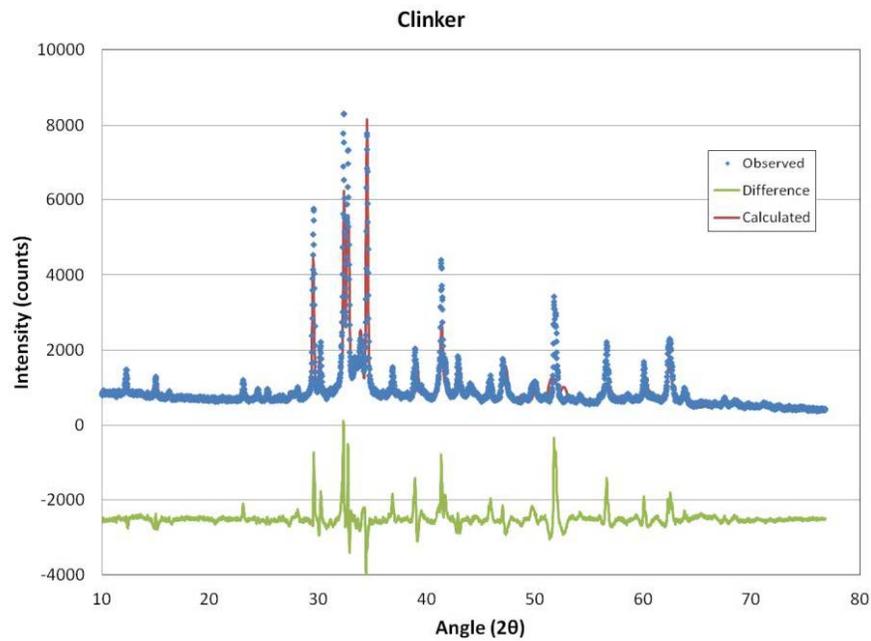
Figure 3. Initial stage of refinement of SRM clinker based upon a single measurement.

Table 3. Phase analysis for clinker sample in Figure 3

Phase	Mass Fraction (%)
Alite	10.68
Belite	43.52
Aluminate	0.00
Ferrite	11.82
Periclase	33.83
Arcanite	0.15
Aphthitalite	0.00

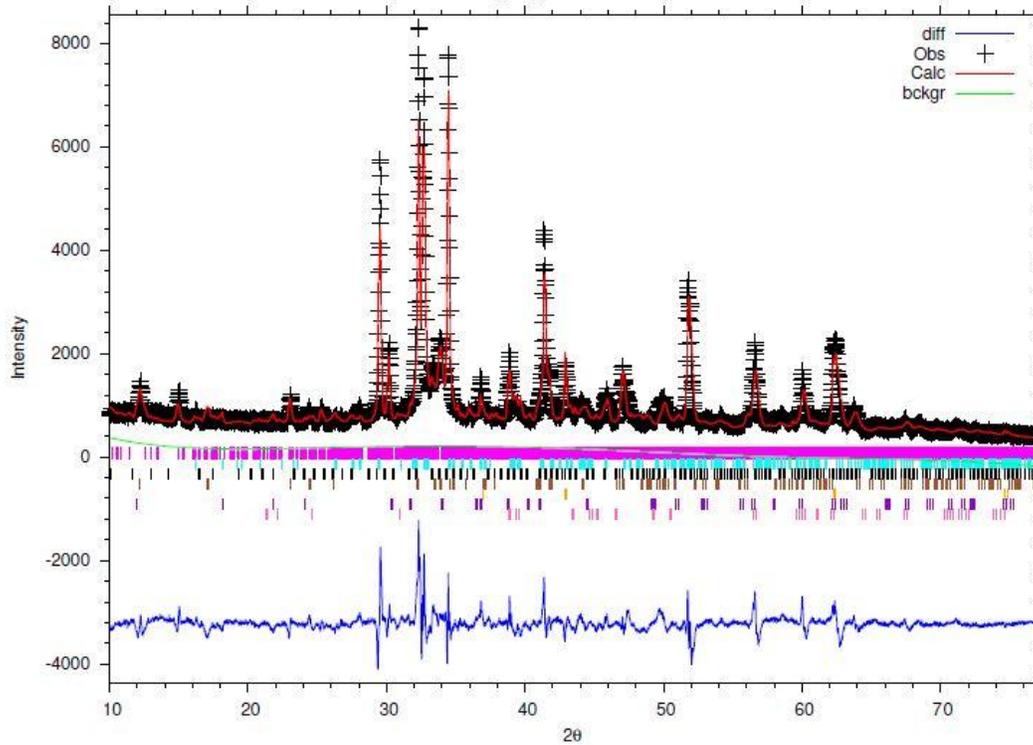**Figure 4. Final Stage of Refinement of SRM clinker.**

Table 4. Phase analysis for the clinker sample in Figure 4

Phase	Mass Fraction (%)
Alite	65.20
Belite	16.85
Aluminate	1.00
Ferrite	12.25
Periclase	4.66
Arcanite	0.05
Aphthitalite	0.12

Additional Exercises

Once you have completed these exercises to your satisfaction, you are ready to use the Rietveld method for quantitative X-ray diffraction analysis of portland clinker and cement using data obtained with your diffractometer.

First create an instrument parameter file for your diffractometer. Obtain, prepare, and run a standard single-phase sample of your choosing (corundum, periclase, lime, and quartz are suitable). Using the crystal structure parameters database, refine the crystal structure parameters and the instrument parameters for this pattern.

Unfortunately, **GSAS** does not transfer refined peak shape parameters when reading from a refined .EXP file, so it is necessary to transfer refined values manually to retain refined peak shapes from previous refined patterns. This is accomplished by selecting the **Profile** tab in **EXPGUI** and editing the peak profile variable values.

Then using the crystal structure parameters provided here and the instrument parameter file for your diffractometer, refine clinker and cement patterns to determine the amount of each phase.

Based on your results with the exercises in these instructions, decide whether or not to use chemical extractions routinely in this analysis.

As you apply this method to your own samples, you will probably develop refinements for crystal structure parameters that provide better fits to the measured data. You can confidently use these refinements as long as you are analyzing samples of a specific chemistry and produced in a specific kiln.

Acknowledgements

References

1. R.A. Young, "Introduction to the Rietveld method", Chapter 1 in *The Rietveld Method*, R.A. Young, ed., Oxford University Press (1995).

2. R.A. Young, editor, *The Rietveld Method*, Oxford University Press (1995).

3. L. Lutterotti, Introduction to Diffraction and the Rietveld method, http://www.ing.unitn.it/~luttero/laboratoriomateriali/RietveldRefinements.pdf (accessed April 6, 2015)

4. A.C. Larson and R.B. Von Dreele, General Structure Analysis System (GSAS), Los Alamos National Laboratory Report LAUR 86-748 (2004).

5. B.H. Toby, EXPGUI, a graphical user interface for GSAS, J. Appl. Cryst. 34, 210-213 (2001).

6. L. Cranswick and I. Swainson, EXPGUI and GSAS Rietveld software practicals, Notes from a workshop at the University of Quebec, (downloaded May 21, 2012 from http://www.cins.ca/cpdw/quebec/ but that link is no longer valid, however the document can be obtained from this link) (2005).

7. http://www.ncnr.nist.gov/programs/crystallography/software/cmpr/cmpr.html (accessed January 26, 2015) and https://subversion.xor.aps.anl.gov/trac/CMPR/wiki (accessed January 26, 2015).

8. B.H. Toby, R factors in Rietveld analysis: how good is good enough, Powder Diffraction 21(1), 67-70 (2006).

9. H.F.W. Taylor, *Cement Chemistry*, 2nd Edition, Thomas Telford (1997).

10. http:/rruff.geo.arizona.edu/AMS/amcsd.php (accessed April 6, 2015).

11. I.C. Madsen, N.V.Y. Scarlett, L.M.D. Cranswick and T. Lwin, "Outcomes of the International Union of Crystallography Commission on Powder Diffraction Round Robin on Quantitative Phase Analysis: samples 1a to 1h", *J. Appl. Cryst.* (2001) 34, 409-426 (http://www.iucr.org/iucr-top/iucr/cpd.html).

12. N.V.Y. Scarlett, I.C. Madsen, L.M.D. Cranswick, T. Lwin, E. Groleau, G. Stephenson, M. Aylmore and N. Agron-Olshina, "Outcomes of the International Union of Crystallography Commission on Powder Diffraction Round Robin on Quantitative Phase Analysis: samples 2, 3, 4, synthetic bauxite, natural granodiorite and pharmaceuticals", J. Appl. Cryst. (2002) 35, 383-400 (http://www.iucr.org/iucr-top/iucr/cpd.html).

13. ASTM 1365, Standard Test Method for Determination of the Proportion of Phases in Portland Cement and Portland-Cement Clinker Using X-Ray Powder Diffraction Analysis, Vol. 4.01 (2006).

14. NIST Certificate of Analysis, Standard Reference Material 2686a, Portland Cement Clinker (2012).

15. P. Stutzman, "Quantitative X-Ray Powder Diffraction Analysis of Portland Cements: Proficiency Testing for Laboratory Assessment," Advances in Civil Engineering Materials, Vol. 3, No. 1, 2014, 21 pp. doi:10.1520/ACEM20130093

Appendix A. Crystal Structure References for Cementitious Materials

A compilation of crystal structure models relevant to portland cement clinker and hydraulic cements have been assembled for use in quantitative X-ray powder diffraction (XRD) analyses by the Rietveld method. These structure models are taken from the literature from single crystal refinements and Rietveld analyses of powder diffraction data and have been transcribed into three different formats: the General Structure Analysis System (GSAS) experiment file (EXP) [4] and the GSAS Table output (TBL), and the Crystallographic Information File (CIF)[3]. The ZIP file, Cements_Data, from http://CIKS … … (need recent WEB address here) should be unzipped in a folder for easy access, keeping in mind that GSAS prefers folder names without spaces. The data are divided into phase groups and by format (.EXP, .CIF, .TBL) within the folder Structures for the crystal structure data as well as diffraction data for clinker and cements (.GSAS).

Structure Data

Phase groups include alite, belite, aluminates, ferrite, alkali sulfate, calcium sulfate, OxCarSil, and Internal Standards, each containing a set of structure models in the GSAS .EXP format that can be read into a refinement project. Appendix B provides a summary of the groups and structures, as well as the individual filename prefixes if you wish to examine the other data formats. For example, if you wish to work with a monoclinic alite structure, refer to the alite phase group where five of the seven structures are monoclinic. The data for the Nishi et al. monoclinic structure may be retrieved by viewing any of the formats using the file prefix MC3S1, or by reading the Alite.EXP file, and selecting the second structure.

The GSAS .EXP file is used to archive structure data for later use through importing data into GSAS, thereby saving the need to manually enter the structure data and are available as individual files using the filename prefix listed in column 4 of Appendix B for each format, or as a collection of structures for specific phase groups, listed under the first column of Appendix B. However, it would be a useful exercise to manually enter structure data for the single-phase diffraction patterns to become familiar with the manual entry procedures.

The Table file (Figure 5) is a readable text file that may be used to check that the CIF or EXP file values were read properly. The CIF file is a standardized but flexible format that most Rietveld codes are capable of reading. If you import these data into another code,

---

[3] http://www.iucr.org/resources/cif

one potential difference may exist concerning the atom thermal (or vibrational) parameters. GSAS uses the U_{iso} or u_{ij} form for vibrational parameters while many other codes utilize the B_{iso} or βij forms, necessitating a transform. GSAS has a provision to perform this conversion within the atom list accessible using the command line via Expedit, following the transforms of $B_{iso}=8\pi^2 U_{iso}$ and $\beta ij = 2\pi^2 a_i * a_j * u_{ij}$ [4]. Check the GSAS manual for additional details if you wish to export them for use in another code. For these exercises, the structure models use the U-forms specified by GSAS.

Diffraction Data

The Powder diffraction data are found in four folders: Test_Phase, containing corundum, free lime, periclase and quartz for the initial single phase analyses, SRM2686, containing three replicate bulk clinker and three selective extraction residue diffraction patterns, and Cement A and B, which contain bulk cement and selective extraction residue data. The diffraction filenames reflect the data type with a SRM or cement number and treatment with bulk specimens (whole clinker or cement) having a filename suffix B, salicylic acid methanol extraction residue data the suffix SAM, potassium hydroxide-sucrose extractions with a suffix KOSH and for some HNO_3 for an extraction residue comprised primarily of the ferrite phase and periclase. Selective extractions concentrate phase groups, providing a clearer diffraction pattern of those phases.

Reading the Table Form (.TBL) Text Files

The GSAS table file is a text file with the pertinent structure data necessary for entering a structure model in GSAS or any other Rietveld code. These data may be used to enter structure models manually or for checking that the values of the CIF file were properly read when importing data.

The GSAS TBL files have the atom vibrational parameters (atom thermal parameters) expressed in the U form as either isotropic or anisotropic, depending on the values reported in the structure data. The CIF files have the vibrational parameters converted to the β form. See page 123 in the GSAS technical manual for additional details on vibrational (thermal) parameters. Key values are highlighted in bold.

Figure 5. Example table file, Corundum.TBL, with key data in bold text.

```
Corundum, alpha Al2O3 after Lewis, Schwarzenbach. Flack, Acta Crys
PUBTABLE Version Win32  Jan 02 08:39:48 2012 Page   1


                  |---------------------------------------|
                  |      Program PUBTABLES Version Win32   |
                  |  Generate crystal structure data tables |
                  | Distributed on Wed Oct 27 21:25:16 2010 |
                  |---------------------------------------|

        |-------------------------------------------------------------|
        |             Allen C. Larson and Robert B. Von Dreele        |
        |        Manuel Lujan, Jr. Neutron Scattering Center, MS-H805  |
        |        Los Alamos National Laboratory, Los Alamos, NM  87545 |
        |                                                             |
        | Copyright, 2000, The Regents of the University of California. |
        |-------------------------------------------------------------|

  GENLES was run on Nov 18 13:50:03 2011    Total cycles run   1


  The Current Least-Squares controls are
  Maximum number of cycles is    3
  I/SigI cut-off is  1.00
  Anisotropic thermal factors are defined by
    T = exp(h**2*astr**2*u11+... +2*h*k*astr*bstr*u12+... )
```

Space group R -3 c
The lattice is centric R-centered trigonal   Laue symmetry 3barm1
 Multiplicity of a general site is 36
 The symmetry of the point 0,0,0 contains 1bar

The equivalent positions are:

(1)	X	Y	Z	(2)	-Y	X-Y	Z	(3)	Y-X	-X	Z
(4)	Y-X	Y	1/2+Z	(5)	-Y	-X	1/2+Z	(6)	X	X-Y	1/2+Z

The CMT file for this cycle was not found.

Lattice constants are
 a = 4.7602000(0) b = A c = 12.9933004(0)
 Alpha = 90   Beta = 90   Gamma = 120
Cell volume = 254.9767151(0)

Name	X	Y	Z	Ui/Ue*100	Site sym	Mult	Type	Seq	Fractn
AL1	0.000000	0.000000	0.352160	0.29*	3	12	AL	1	1.0000
O2	0.306240	0.000000	0.250000	0.35*	2(100)	18	O	2	1.0000

Thermal parameters multiplied by 100.0 are

Name	U11	U22	U33	U12	U13	U23
AL1	0.28	0.28	0.30	0.14	0.00	0.00
O2	0.33	0.34	0.37	0.16	0.05	0.09

Appendix B. GSAS Experiment files for selected phase groups and structures.

Phase Groups	Phase	Reference	Filename
Alite.EXP	Triclinic	N. Golovastikov, R. Matveeva, N. Belov Kristallografiya, (1975) Vol. 20, pp. 721-729	TC3S1
	Monoclinic	F. Nishi, Y. Takeuchi, and I. Maki, Zeit. Krist., (1985) Vol. 172, No. 3-4, pp. 297-314	MC3S1
	Monoclinic (M1)	M.-N de Noirfontaine F. Dunstetter, M. Courtial, G. Gasecki, and M Signes-Frehel, Cem. Conc. Res., (2006) 36 54-64	ALITE_M1
	Monoclinic (M3)	M.-N de Noirfontaine F. Dunstetter, M. Courtial, G. Gasecki, and M Signes-Frehel, Cem. Conc. Res. (2006) 36 54-64	ALITE_M3
	Monoclinic	A.G. De La Torre, S. Bruque, J. Campo, and M.A.G. Aranda, Cem. & Conc. Res. (2002) 32, 1347-1356	MC3S3
	Monoclinic	W.G. Mumme, N. Jb. Miner. Mh., (1995) No. 4, pp. 145-160	MC3S4
	Rhombohedral	F. Nishi and Y. Takéuchi, Zeit. Krist., (1984) 168, 197-212	RC3S1
Belite.EXP	Beta	K.H. Jost, B. Ziemer, and R. Seydel, Acta Cryst. (1977) B33, 1696-1700	BC2S3
	Beta	W.G. Mumme, R.J. Hill, G. Bushnell-Wye, and E.R. Segnit, Neues Jarb. Mineral. Abh. 169 (1995) 35-68	BC2S2
	Alpha	W. Eysel and T. Hahn, Zeit. Krist.,(1970) 131,322-341	AC2S3
	Alpha Prime, high	W.G. Mumme, R.J. Hill, G. Bushnell-Wye, and E.R. Segnit, Neues Jarb. Mineral. Abh. 169 (1995) 35-68	APHC2S
	Alpha Prime, low	A.M. Il'inets and M.Ya. Bikbau, Kristallografiya (1990) 35, 91-93	APLC2S1
	Gamma	S. Udagawa, K. Urabe, M Natsume, and T. Yano, Cem. and Conc. Res., (1980) Vol.10, No. 2, 139-144	GC2S2
	Gamma	D.K. Smith, A. Majumdar, and F. Ordway, Acta Cryst. (1965) Vol. 18, 787-795	GC2S3
Aluminate.EXP	Cubic	P.Mondal & J.W.Jeffery, Acta Cryst. (1975) B31, 689-697	CUBC3A1
	Cubic	Y. Takeuchi, F. Nishi and I Maki, Zeit. Krist. (1980) 152, 259-307	CUBC3A3
	Cubic	R. Berliner, C. Ball, and P.B. West, Cem. Conc. Res., (1997) Vol. 27, No. 4, pp. 551-575	CUBC3A2
	Orthorhombic	R. Berliner, C. Ball, and P.B. West, Cem. Conc. Res., (1997) Vol. 27, No. 4, pp. 551-	C3AORT1

		575	
	Orthorhombic	Y. Takeuchi, F. Nishi and I Maki, Zeit. Krist. (1980) 152, 259-307	ORTC3A1
	Orthorhombic	F.Nishi and Y. Takéuchi, Acta Cryst. (1975) B31, 1169-1173	ORTC3A2
	Orthorhombic	V.Kahlenberg R.X. Fischer, and C.S.J. Shaw, Am. Miner. (2000) Vol. 85, 1492	C4A3-1
	Monoclinic	Y. Takéuchi, F. Nishi, and I. Maki, Zeit. Krist. (1980) 152, 259-307	MC3A1
	Monoclinic	Y. Takéuchi, F. Nishi, and I. Maki, Zeit. Krist. (1980) 152, 259-307	MC3A2
Ferrite.EXP	Orthorhombic	A.A. Colville and S. Geller, Acta Cryst. (1972) B28, 3196-3200	C4AF4
	Orthorhombic	R. Berliner, C. Ball, and P.B. West, Cem. Conc. Res., (1997) Vol. 27, No. 4, pp. 551-575	C4AF
AlkaliSulfate.EXP	Arcanite, beta	J.A. McGinnety, Acta Cryst. B28, (1972) 2845 -2852	K2SO4B1
	Arcanite, beta	M.T. Robinson, J. Phys. Chem., (1958) 62, 925-928	K2SO4B2
	Arcanite, beta	R.W.G. Wyckoff, Crystal Structures, Wiley, 1963	K2SO4B3
	Arcanite, alpha	A.J. van den Berg and F. Tunistra, Acta Cryst. (1978) B34, 3177-3181	K2SO4A1
	Aphthitalite	K. Okada and J. Ossaka, Acta Cryst. (1980) B36, 919-921	APHTHI1
	Aphthitalite	K. Okada and J. Ossaka, Acta Cryst. (1980) B36, 919-921	APHTHI2
	Langbeinite	R.W.G. Wyckoff, Crystal Structures, Wiley, 1963	LANG1
	Metathenardite	W.Eysel, H.H. Höfer, K.L. Keester, and Th. Hahn, Acta Cryst. (1985) B41, 5-11	METATH1
CalciumSulfate.EXP	Gypsum	M. Atoji and R.E. Rundle, J. Chem. Phys. (1958) Vol. 29, No. 6, 1306	GYPSUM1
	Gypsum	B.F. Pedersen and D. Semmingsen, Acta Cryst. (1982) B38, 1074-1077	GYPSUM2
	Gypsum	W.F. Cole and C.J. Lancucki, Acta Cryst. (1974) B30, 921-929	GYPSUM3
	Anhydrite	A. Kirfel and G. Will, Acta Cryst. (1980), B36, 2881-2890	ANH1
	Anhydrite	F.C. Hawthrone and R.B. Ferguson, Canadian Miner. (1975), V.13, 289-292	ANH2
	Anhydrite	H. Morikawa, I. Minato, T. Tomita, and S. Iwai, Acta Cryst. B31, (1975), 2164-2165	ANH4
	Soluble Anhydrite	C. Bezou, A. Nonat, and J. –C. Mutin, Journal Solid State Chem. (1995), 117, 165-176	ANH3
	Bassanite	P. Ballirano, A. Maras, S. Meloni, and R. Caminiti, Eur. Jour. Min. (2001), Vol 13, No. 5, 985-993	Bassanite1
	Bassanite	W. Abriel, R. Nesper, Zeit. Krist. (1993), 205, 99-113	Bassanite2

Ox_Si_Car.EXP	Periclase	R.W.G. Wyckoff, <u>Crystal Structures</u>, Wiley, 1963	Periclase
	Free Lime	R.W.G. Wyckoff, <u>Crystal Structures</u>, Wiley, 1963	Lime
	Quartz	L. Levien C.T. Prewitt, D.J. Weidner Am. Min. (1980) Vol. 65 pp. 920-30	Quartz
	Calcite	S.A. Markgraf, R.J. Reeder, Am. Min. (1985) Vol. 70, pp. 590-600	Calcite
	Mg Calcite	P.L. Althoff, Am. Min. (1977) Vol. 62, pp. 772-83	MgCalcite
	Dolomite	P.L. Althoff, (1977) Am. Min. Vol. 62, pp. 772-83	OxCarSil (phase 5)
InternalStandard.EXP	Corundum	J. Lewis, D. Schwarzenbach,and H.D. Flack, Acta Cryst. (1982), (A38), 733-739	Corundum
	Rutile	E.P. Meagher and G.A. Lager, Can. Min., (1979), V. 17, pp. 77-85	Rutile
	Zincite	R.W.G. Wyckoff, <u>Crystal Structures</u>, Wiley, 1963	Zincite