Fundamentals of Rietveld Refinement
III. Additional Examples

An Introduction to Rietveld Refinement
using
PANalytical X'Pert HighScore Plus v3.0d

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We are going to determine the phases present in a mixture and then refine that mixture

- These exercises will remind you of what we did previously and demonstrate a few extra features

- The steps for this exercise:
1. Enable the COD database
2. Determine what phases are present in this sample
3. Perform a Rietveld refinement of the mixture

Adding a Database to HighScore Plus

- The free COD database was downloaded from http://www.crystallography.net/new.html
  - Alternatively, you may have installed the ICDD PDF4 database
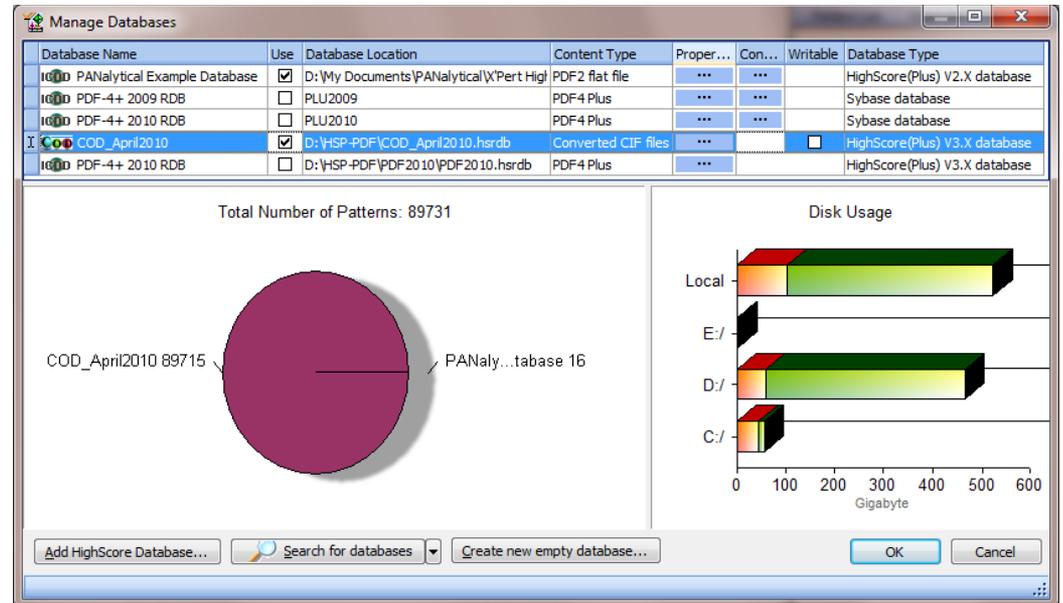
- In HighScore Plus, go to menu *Customize > Manage Databases*
- Click on **Add HighScore Database**
- Navigate and select the COD database with a *.hsrdb extension
- Make sure that the **Use** column is checked
  - If the Writable column is checked, you will be able to add your own entries to the database

Phase Identification: fit the background

1. Open the file "hydrated abalone.xrdml"
2. Fit the background
   – Set the y-axis to square root scale
   – Select menu *Treatment > Determine Background…*
     - Use Granularity between 10 to 30
     - Use Bending Factor 0 or 1
     - Click **Accept**;
       – never ever Subtract the background
         » Unless you really want to
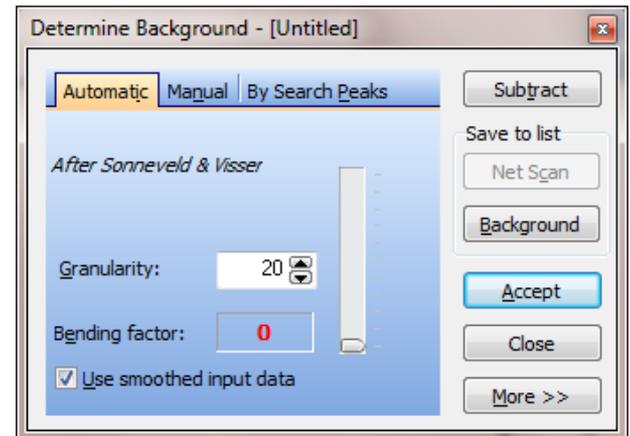
Phase Identification: Peak Search

3. Locate the diffraction peaks
   - Select menu *Treatment > Search Peaks…*
   - Use the "Identify" parameter set
     - Click on the **More** button
     - Select **Identify** from the drop-down menu
   - Click on the **Search Peaks** button
   - Evaluate the Results
     - Modify the search parameters and click **Search Peaks** again
     - If the search results are good, click on the **Accept** button
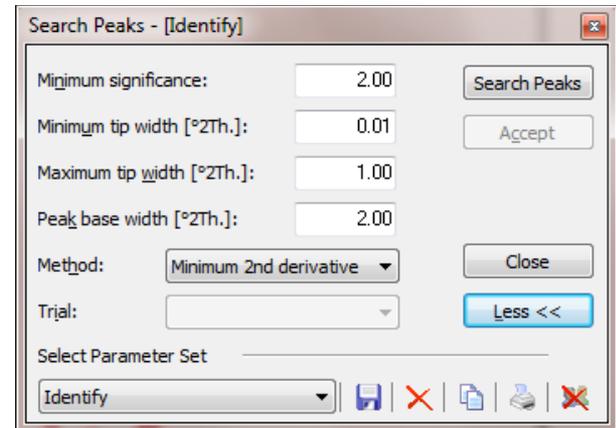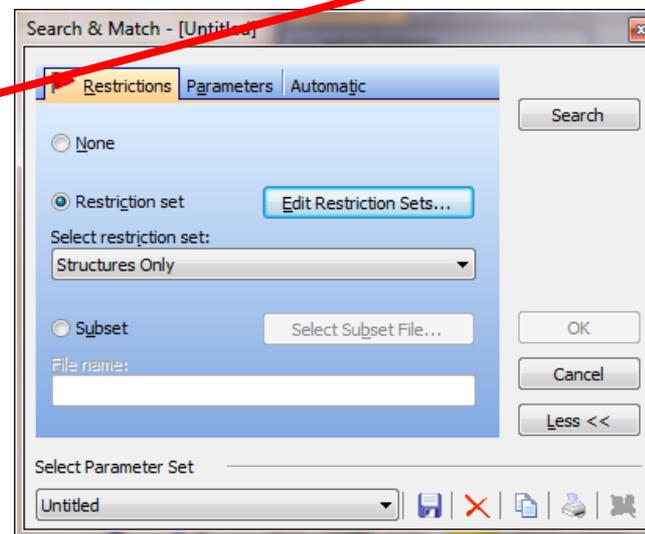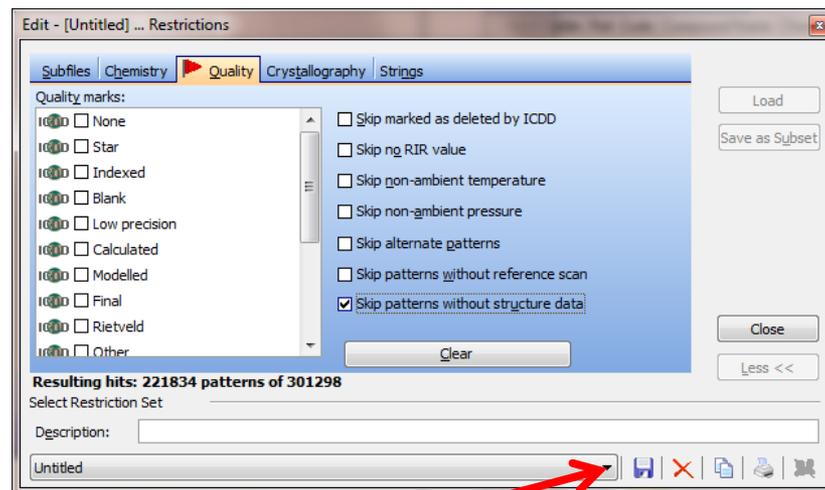
Phase Identification: Run the Search & Match

- Run the phase identification Search & Match algorithm
- Select menu *Analysis > Search & Match > Execute Search & Match*
  - Use the "Default" parameter set to start
    - Click on the **More** button
    - Select **Default** from the drop-down menu
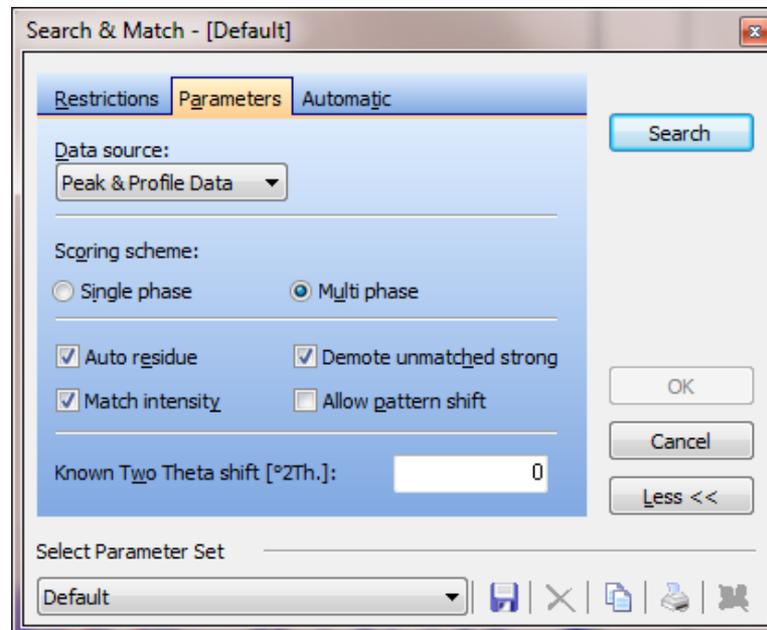
We are going to create a Search & Match routine that only retrieves reference patterns that contain crystal structures that can be used in our Rietveld refinement

- Click on the <u>Restrictions</u> tab
- Select the **Restriction set** radio button
- Click on the **Edit Restriction Sets** button
- In the new window that opens, select the <u>Quality</u> tab,
- Check "Skip patterns without structure data"
  - You might also want to check
    - Skip non-ambient temperature
    - Skip non-ambient pressure
- Save the Restrictions Parameter Set
  - Click on the floppy disk icon
- Click **Close**
- Save the Search & Match Parameter Set
 - Click on the floppy disk icon

Phase Identification: Determine Good Matches

- Click on the **Search** button
- Click **OK** when the search is done
- Look through the candidate list and determine if any of the highest scored phases are a good match
- If they are, then move them to the Accepted Pattern list
- The program automatically rescores the candidates
  - you should find another match at the top of the newly resorted candidate list
- Once you have identified all of the relevant phase, clear the candidate list
  - Right-click in the candidate list
  - Select **"Remove All Candidates"**
  - This will speed up the program

Need more help with Search & Match procedures?

- In the HELP, look under the *Quick Start Guide*
  - Performing Search-Match Identify
  - Phase Identification Strategy
  - You may also have a printed copy of the *Quick Start Guide*
- In the HELP, look under *Analysis > Phase Analysis*
- Online, look at http://www.icdd.com/resources/tutorials/
  - Data Mining- Trace Phase Analysis
  - Other tutorials
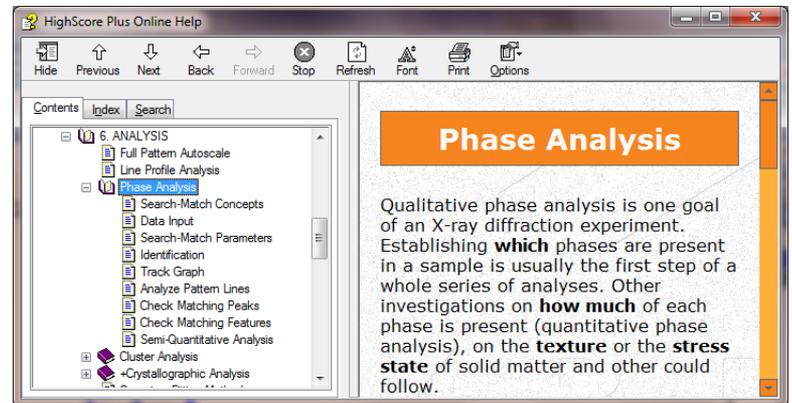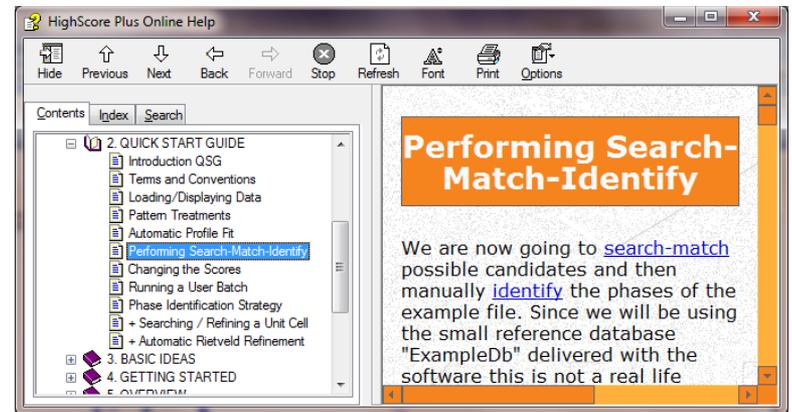
Refining a sample with two phases present

- Our Phase ID shows that both aragonite and calcite phases are present

- Set refinement mode to "Semi-Automatic"
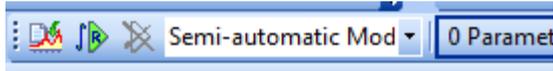
- We need to transfer the crystal structures from the reference cards into our refinement control
  - In the <u>Pattern List</u>, select both phases
    - Select multiple phases by using Shift + Click
  - Right-click in the <u>Pattern List</u> and select "**Convert Pattern to Phase**"
  - Select <u>Refinement Control</u> in the Lists Pane
    - You will see that aragonite and calcite have been entered into the refinement control

# Global Parameters in the refinement will affect both phases

- The Global Parameters will affect both phases
  - background
  - specimen displacement or zero shift
  - POL correction
- Phase parameters are refined separately for each phase

- We are going to use the background that we manually fit in order to make the refinement a little easier
  - Select Refinement Control tab in the Lists Pane
  - Click on "Global Variables"
  - In the Object Inspector, under Background set the method to "**Use Available Background**"
  - This approach works very well for complex mixtures or diffraction patterns that have a lot of overlapping peaks

Shortcut for refining parameters from multiple phases

- Right-click on any field in the <u>Refinement Control</u> list
- The "**Refine All**" and "**Fix All**" choices will set refinement of a parameter for all of the phases loaded into the refinement model
- Remember, you can use "**Show Refined Values/Constraints...**" to keep track of all of the parameters that are currently being refined
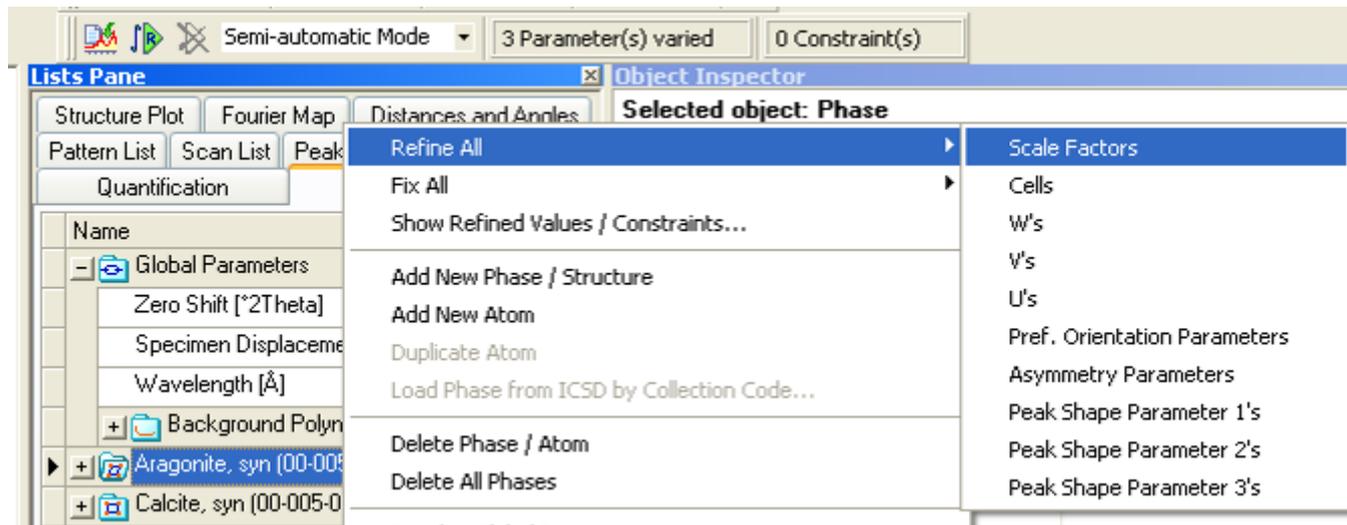
The refinement of multiple phases proceeds similarly to that of single phases

1. Refine the scale factor for both aragonite and calcite
   1. Right-click on any field in the <u>Refinement Control</u> list
   2. select *Refine All > Scale Factors*
   3. Click on the **Start Rietveld Refinement** button
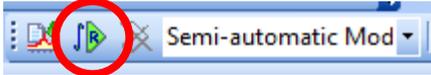
2. Refine 'Specimen Displacement' to adjust peak positions
   1. In the Global Variables field of the <u>Refinement Control</u> list, put a check mark next to **Specimen Displacement**
   2. click on the Start Rietveld Refinement button

Excluding problematic regions to improve the refinement

- Background at high angles doesn't fit so well
- we can either try fitting it or ignore it
- We will ignore it
  - Select menu *Analysis > Rietveld > Edit Excluded Regions*
  - Click **New Region**
    - type 68 for start
    - type 70 for end
  - click **OK**
- Run the refinement again without adding additional refinement terms
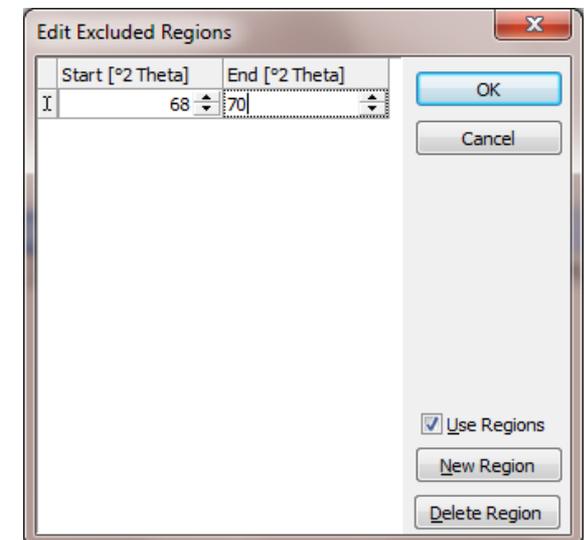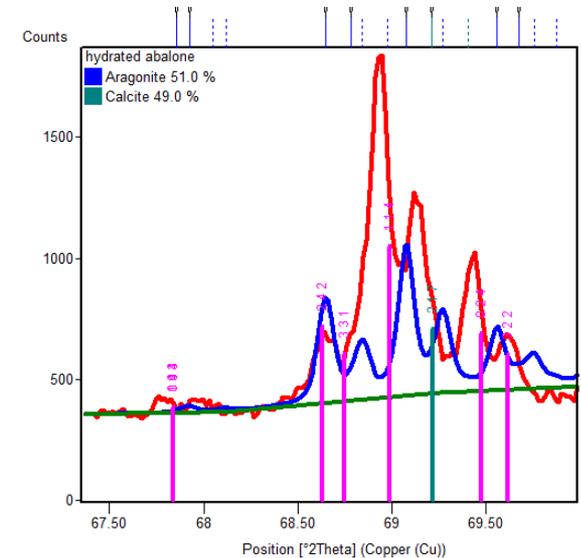
# Refining parameters for individual phases requires some consideration

- Refining Lattice Parameters– should the sample have similar or different lattice parameters from those in the initial crystal structure?
    - this sample is from the shell of abalone, a sea snail
    - crystal structures from NBS data for synthetic analogues to the mineral
    - it would be reasonable for the lattice parameters to be *slightly* different
- If the lattice parameters from the initial structure should be accurate to the sample in consideration, then maybe refine the profile parameters before refining the lattice parameters

- In this case, we will refine the lattice parameters for both phases
    - right-click in the Refinement Control list
    - select *Refine All > Cells*

Refining peak profiles in multiphase samples should be done cautiously if there are a lot of overlapping peaks

- Sometimes, Rietveld refinement code will make the peaks from one phase very wide
  - The code is trying to use a wide peak from phase 1 to account for intensity from phase 2
  - Sometimes, the code tries to improve a poor fit to the background by making the diffraction peaks very wide

- refine W, V, and U for both phases
  - refine each Cagliotti peak width parameter one at a time
  - again, using the "Refine All" and "Fix All" options can save a lot of time

- refine Peak Shape Parameter 1

Evaluate the Quality of the Refinement

- Evaluate the refinement
  - how good is it?
  - The Weighted R profile is ~22%
    - The R expected is 2.6%
  - when you click on a phase name in the <u>Refinement Control</u> list, you will see a highlighted trace emphasizing that phase alone
    - If this does not work, select menu *View > Display Mode > Show Selected Phase Profile*
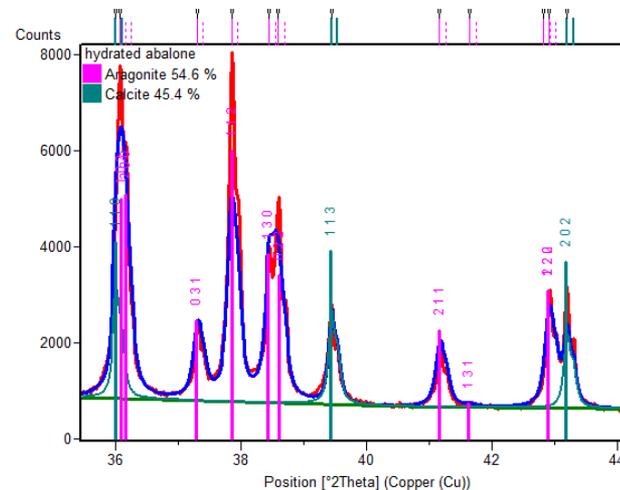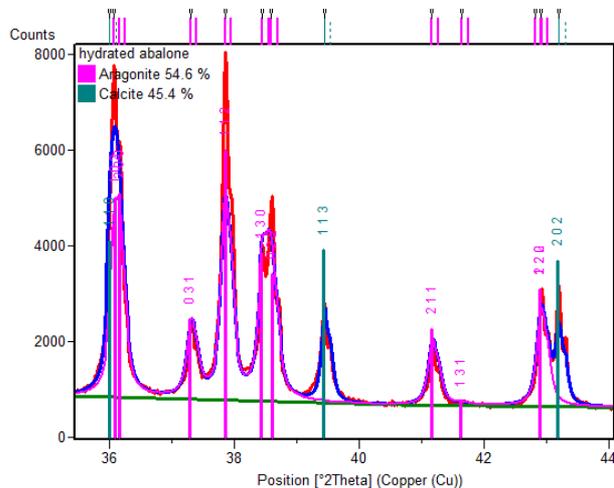
Problems with Refinement

- Aragonite
  - peaks at 31deg (002) and 33deg (012) for aragonite do not have enough intensity
  - suggests [002] preferred orientation

- Peak profiles do not vary properly
  - high angle peaks in experimental data are sharper than as fit with simulation

- If you refine B Overall for both samples, the B for calcite is much larger than for aragonite
  - this sort of thing often suggest sample preparation problems

- For all of these problems, once the preferred orientation is accounted for the calculated weight fractions for the mixture is good

Let's refine another sample

1. In <u>Refinement Control</u>, right-click and select *Fix All > Refined Parameters*
2. Select the <u>Scan List</u>
3. Right-click on the scan and select *Remove Scan*
4. insert dry abalone.xrdml
   1. Select *File > Insert*
5. Fit the background
   1. Select *Treatment > Determine Background*
6. Select the Refinement Control List
   1. Both phases are still present in the Refinement Control List
7. Refine scale factor for both phases
8. Refine specimen displacement
- without much work, what do we learn about this sample?

- If we were interested in investing more time for this analysis, a good approach would be:
  - refine the aragonite structure in the dry abalone data file, since the single phase sample will be much easier to refine than the mixture
  - feed the phase parameters (lattice parameters, preferred orientation, B overall, profile parameters, etc) for aragonite from the single phase dry abalone sample into the refinement of the mixture in hydrated abalone sample

Using Automatic Rietveld Refinement in HSP

- We are going to refine $PbTiO_3$ data using an automated batch

- Open "PbTiO3 RT.xrdml"

- Instead of creating a crystal structure from scratch, we are going to load a crystal structure from an external file
  - go to *File > Insert*
  - select PbTiO3.cry
    - the *.cif format is more common for data downloaded from online journals and databases
    - the cry format can be created by HSP and can contain multiple crystal structures
  - The PbTiO3.cry file contains the crystal structures for both tetragonal and cubic forms of PbTiO3
  - load just the tetragonal form

Automatic Rietveld Refinement

- You can use automatic fitting to progress through the initial refinement steps without having to do it all manually
- Set up automatic Rietveld Refinement
  - *Analysis > Rietveld > Edit Automatic Rietveld Steps*
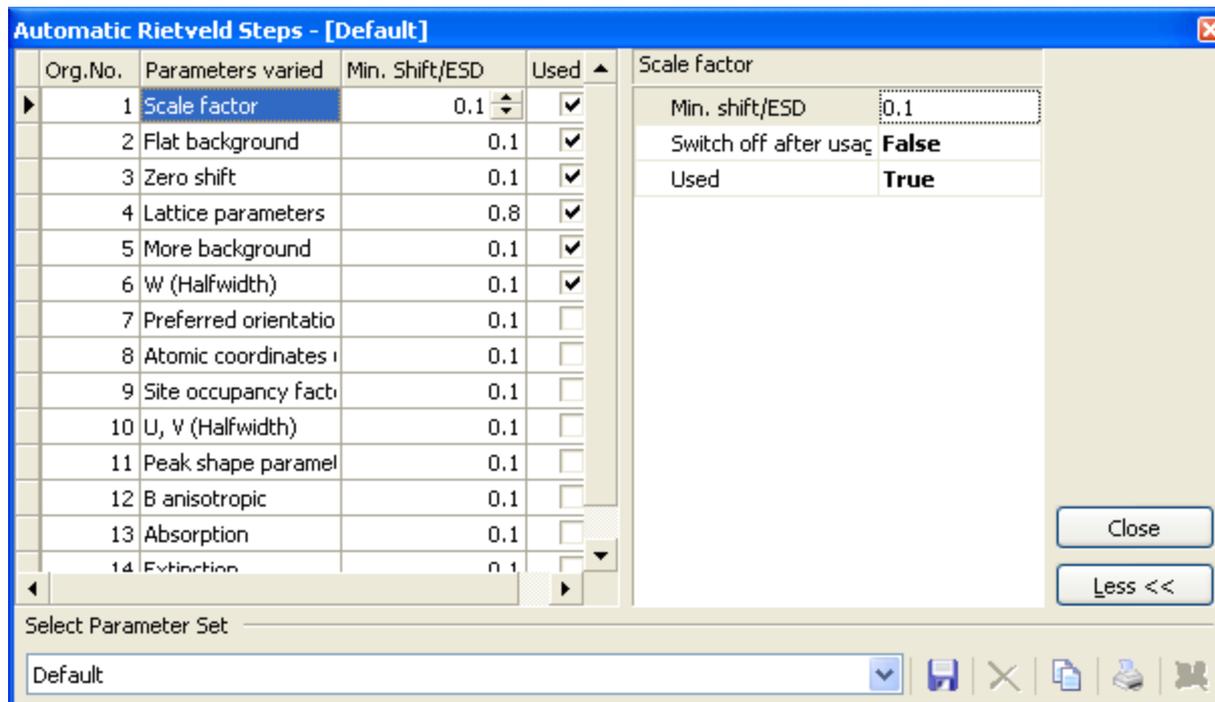
- You can reorder steps in the Automatic Rietveld program by drag and dropping
- Check the "Used" column to indicate if that step will be executed or not
- there are additional details for each step that can be modified
  - the biggest choice for all of the is the "Switch off after usage" flag, which determines if that parameter continues to be refined as refinement proceeds to the next step or if it fixed during all subsequent steps
- Click the **More>>** button to see the controls for loading parameter sets and for saving your custom parameter set

Automatic Rietveld

- Parameters in the Automatic Rietveld program
  1. Scale Factor:
     - SwitchOffAfterUsage: False →

     continue refining this parameter as additional parameters are also refined

  2. Flat Background:
     - SwitchOffAfterUsage: False
  3. Zero Shift:
     - Refine Specimen Displacement Instead: True →

     only refine one or the other; specimen displacement is almost always the better choice

     - SwitchOffAfterUsage: False
  4. Lattice Parameters:
     - Minimum Weight Percentage:5 →

     many parameters should not be refined for trace phases because the peaks are too weak; -1 means no minimums are applied

     - SwitchOffAfterUsage: False
  5. More Background:
     - No. of Additional Background Parameters: 2 (can be 1-5)
     - SwitchOffAfterUsage: False

6. W (Halfwidth)
   - Minimum Weight Percentage: 5
   - SwitchOffAfterUsage: False
7. U, V (Halfwidth)
   - Minimum Weight Percentage: 10
   - Refine U: True
   - Refine V: True
   - SwitchOffAfterUsage: True

if you have instrument parameters for initial u, v, and w values, then consider not refining v; especially if evaluating nanocrystallite size

8. Peak Shape Parameters
   - Minimum Weight Percentage: 10
   - No of Parameters: 1
   - Refine Anistropic Broadening: False
   - Refine Asymmetry: False
   - SwitchOffAfterUsage: True
9. Site Occupancy factor and B isotropic
   - Minimum Atomic Number: 20

don't automatically refine values for light elements

   - Minimum Weight Percentage:10
   - Refine Mixed Sites: False
   - SwitchOffAfterUsage: False
   - Use Overall B: True

- Save the Automatic Rietveld parameter set
  - button in the lower right corner might say "More"
  - click on this button to see the options for saving the parameter set
  - click on the floppy disk icon to save the parameter set
- To run the Automatic Rietveld refinement using the saved parameter set
  - set the Refinement mode to "Automatic Mode"
  - click on the drop-down menu next to the "Start Refinement" button
  - choose the parameter set that you saved
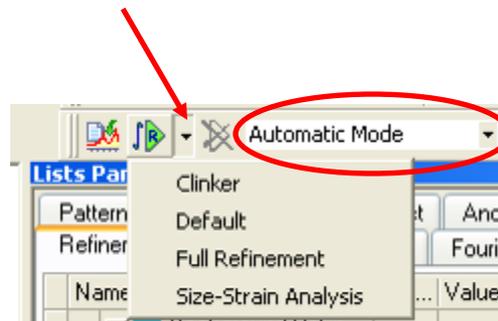
- The automatic mode refinement gets us 95% of the way to the solution with this example
  - the weighted R profile is near 10%

- This approach can be very effective for routine quantitative phase analysis

- To improve the refinement, we could change the refinement mode to semi-automatic mode and do some manual refinements
  - the biggest improvement would come from refining some of the profile parameters together and by refining the asymmetry parameter

1. Crystallite Size Analysis
    1. Refining an instrument profile standard
    2. Using the result to create a template
    3. Refining a nanocrystalline sample
    4. Improving the refinement by using LeBail fitting

Using a template for nanocrystallite size analysis

- We are going to refine a Ceria (CeO_2) standard
- This will be used to determine the U, V, and W that is characteristic for the instrument profile of our diffractometer
- We will use the result to create a template that can then be used in the analysis of nanocrystalline Ceria

- Open Ceria Standard.xrdml
- Insert Ceria Structure.cif
- Refine the model

Use the results of the previous refinement to create instrument profile parameters

- In the <u>Refinement Control</u> list, right-click on the phase name
  - you need to click on the phase name, not on any other field
  - select "Take as Size-Strain Standard"
  - this exports the U, V, and W values into the Global Parameters object as U standard, V standard, and W standard
  - these values will be used to determine how a sample profile is broadened due to crystallite size and/or microstrain
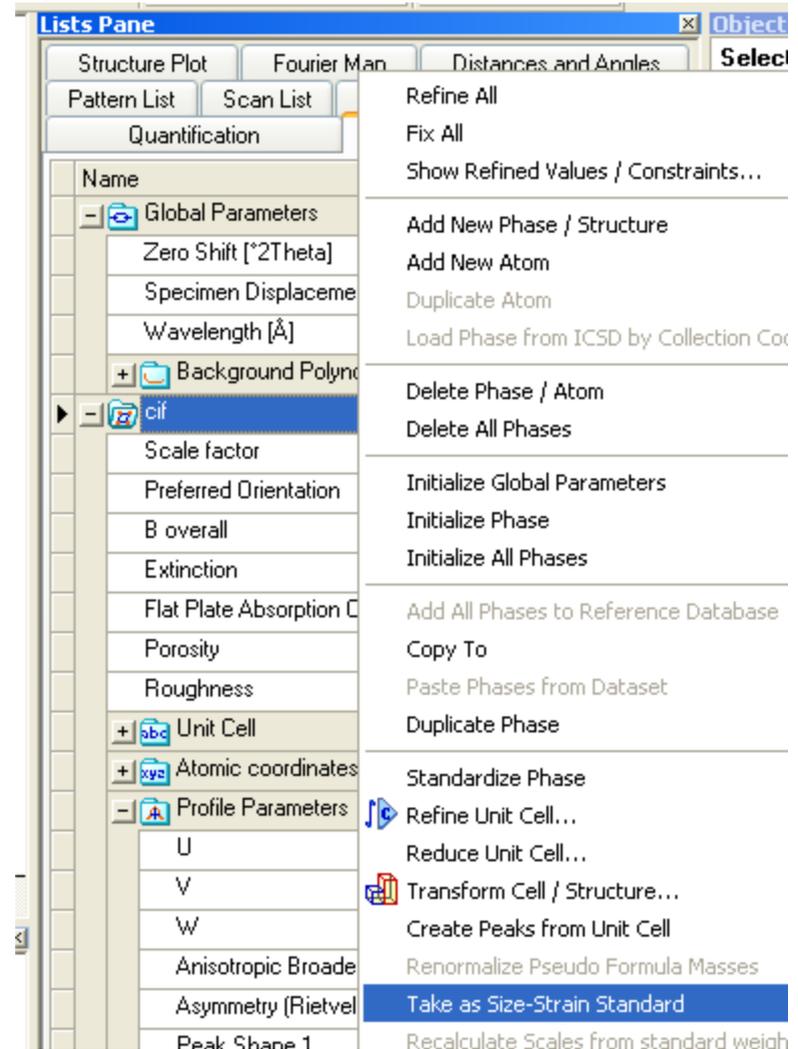
A template can be used as a starting point for multiple analyses of experimental data

- You could record the Caglioti coefficients from the Instrument Standard field and them enter into every new document
  - If you are not sharing a computer and only use one instrument with one configuration, you could also save them as defaults in the menu *Customize > Defaults*

- In order to save work, you can also create a template file
  - A template file is an empty HPF document that contains several settings
  - We will create a document that contains the Caglioti coefficients determined by the analysis of the standard
  - A template can also contain
    - Reference patterns
    - Peaks in the peak list
    - Phases for refinement

Creating a template

- After you create the Size-Strain Standard
  - Go to the <u>Peak List</u> tab in the Lists Pane
    - Right-click in the <u>Peak List</u> and select the menu option *Delete > Included Peaks*
  - Go to the <u>Refinement Control</u> tab in the Lists Pane
    - Expand the entries Global Variables and Background
    - In every parameter within Background (Flat Background, Coefficient 1, etc), set the value to 0
    - Remove the Phases if your specimen is a different material
  - Go to the <u>Pattern List</u> in the Lists Pane
    - Delete all reference patterns loaded in the <u>Pattern List</u>
    - If you are always analyzing the same phase(s), you could load the reference patterns for those phases and save them in the template
  - Go to the <u>Scan List</u> in the Lists Pane
    - Delete all experimental scans loaded in the <u>Scan List</u>
- Save the document in a *.HPF format with a clever name like "LP Analysis Template.hpf

To determine the crystallite size, you need to specify the sample broadening analysis for each phase

- To analyze the nanocrystalline specimen, insert the file "ceria nanophase.xrdml" into the template file
- Go to the <u>Refinement Control</u> list
- Click on the phase name for the ceria structure
- In the Object Inspector, find the Phase Profile area
- In the field Size Strain Analysis, from the drop-down menu you should select either "Size Only" or "Size and Strain"
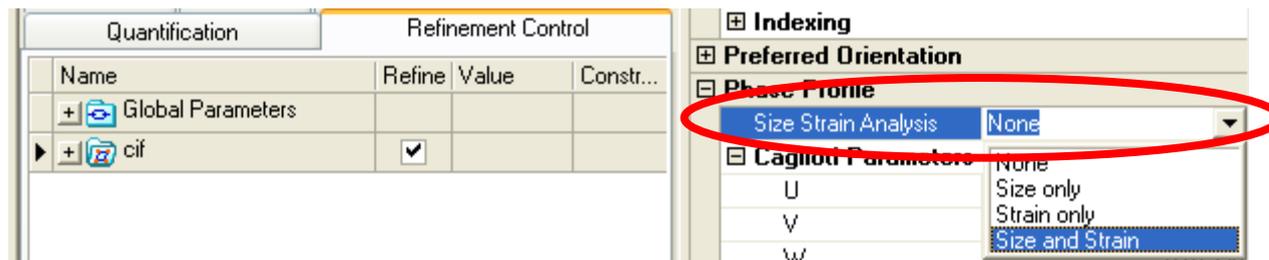
Refine the sample to determine the crystallite size

- The Cagliotti parameters will be used to determine how size and strain creates broadening of the sample
  - V will not be refined
  - U and W will be refined according to the Size-Strain analysis specific in the phase settings
- After refinement, you can find the calculated size and/or strain from in the Object Inspector for the phase, under Derived Data
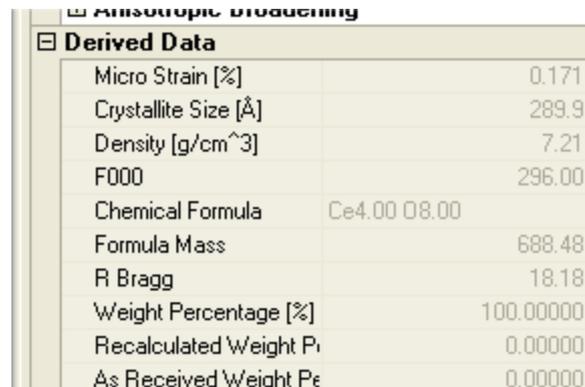
Derived Data	
Micro Strain [%]	0.171
Crystallite Size [Å]	289.9
Density [g/cm^3]	7.21
F000	296.00
Chemical Formula	Ce4.00 O8.00
Formula Mass	688.48
R Bragg	18.18
Weight Percentage [%]	100.00000
Recalculated Weight P	0.00000
As Received Weight Pe	0.00000

Templates can be used to facilitate analysis of a number of sample types

- For QPA of mixtures, refine a mixture and save the result as a template
  - this will preserve the refined lattice parameters, peak profiles parameters, and preferred orientation coefficient
  - using this as a starting point for analysis of similar mixtures can make it faster

# Fixing the ceria refinement using LeBail (structureless) fitting

- Because of poor sample preparation, the intensity does not vary properly as a function of 2theta
  - the experimental intensity at large angles 2theta are incorrect

- We can accurately determine lattice parameters and crystallite size broadening even if the intensity is off
  - this assumes that the errors affecting intensity do not affect the peak positions or peak profiles

- To fit data with a systematic error in intensity, we will arbitrarily fit the intensity of each peak
  - instead of calculating the intensity from the structure factor from the crystal structure of the phase

To start the LeBail fit

- click on the phase name in the <u>Refinement Control</u> list
  - In the General Phase Info field of the Object Inspector change the fitting mode from **Structure Fit** to **Le-Bail Fit**
- Right-click on any field in the <u>Refinement Control</u> list
  - select "Fix All"
  - select "Refined Parameters"
- Run a refinement in Semi-automatic mode
- This iteration of refinement is used to fit the intensity of each individual peak
  - peak positions and peak profiles are still constrained by the parameters of the phase, such as lattice parameter and Cagliotti parameters

Preferred Orientation

- First, identify the direction of the preferred orientation
  - Begin the Rietveld refinement of the data
  - Turn on (hkl) labelling of peaks
    - Right-click in the Main Graphics window and select Label Peaks
    - In the Label Peaks dialog, select HKL
    - Click OK
    - The peaks will now be labelled
    - This only works if the calculated pattern has been simulated or refined
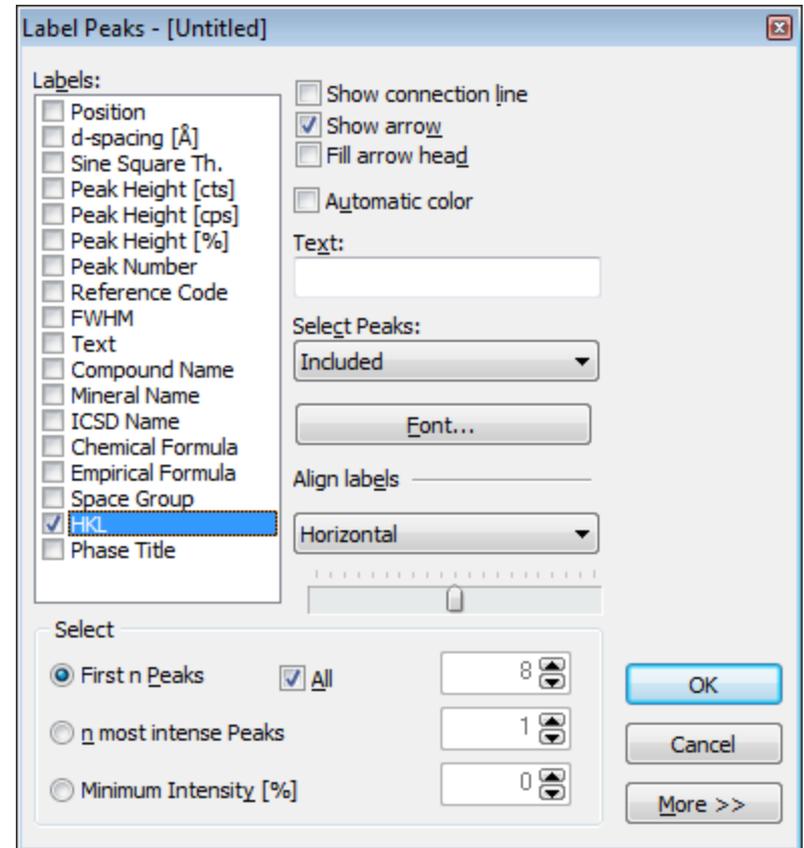
Preferred Orientation

- Look at the (hkl) values for obvious trends in intensity vs. geometry
  - Remember that (hkl) is parallel to (n*h n*k n*l)
  - For example, (011) and (022) are parellel
  - In the plot to the right, the (011) and (022) peaks are both stronger than calculated
  - All other peaks are weaker than calculated
  - This indicates a [011] preferred orientation
  - Sometimes a related set of peaks will be weaker rather than stronger; this corresponds to a needle-like particle shape
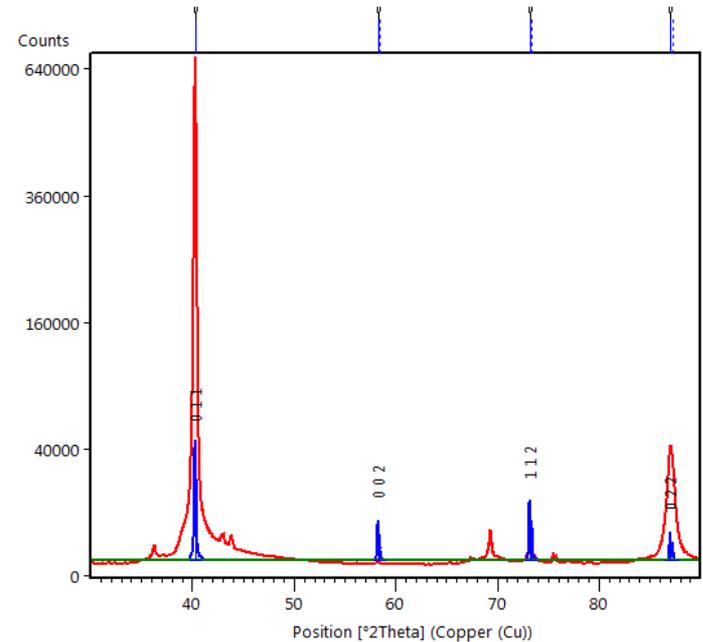
Defining Preferred Orientation with the March-Dollase function

- March-Dollase is defined assuming one axis is fixed in its orientation and the other two axes have freedom of rotation
  - If the March-Dollase parameter is <1, then the fixed axis is normal to the surface of the sample (parallel to the diffraction vector s) and [hkl] is defined as the fixed axis which will produce diffraction peaks stronger than otherwise predicted
  - If the March-Dollase parameter is >1, then the fixed axis is parallel to the surface of the sample (normal to the diffraction vector s) and [hkl] is defined as the fixed axis which will produce diffraction peaks weaker than otherwise predicted

Set the preferred orientation direction in the Object Inspector window for the selected phase

Flag the preferred orientation parameter to refine here

Set the preferred orientation direction here