Rietveld Analysis Workshop
Example 2
Multiphase analysis

Introduction

In this example you will quantitatively analyse a biphasic mixture using X-ray powder diffraction data. The mixture contains 14.53 wt% calcite ($CaCO_3$) and 85.47 wt% monetite ($CaHPO_4$). Data were collected on a PANAlytical X'Pert Pro diffractometer in Bragg-Brentano geometry using Ni filtered Cu-Kα radiation. The following files are required.

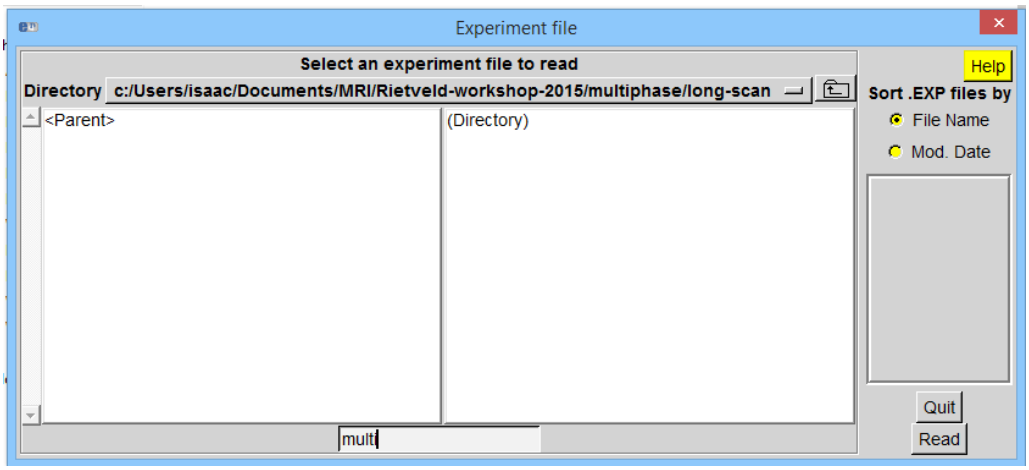
XPA9109.gda	Powder diffraction data in GSAS GDA format
XPA9109.xrdml	Powder diffraction data in PANAlytical xrdml format
xpert2.prm	Instrument parameter file
calcite_CaCO3_18166.cif	cif file for calcite
monetite_CaHPO4_87196.cif	cif file for monetite

Create a working directory wherever you want.

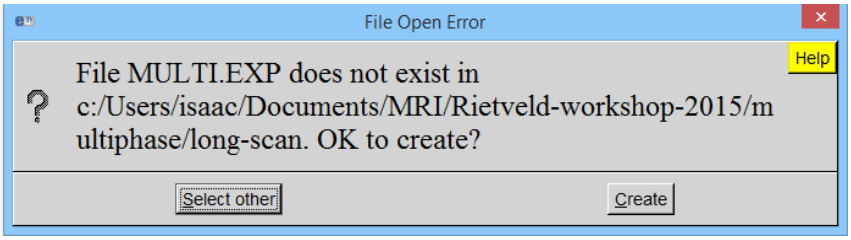
Copy the files listed above into the working directory

Start **Expgui** and navigate to the working directory where you have placed the files

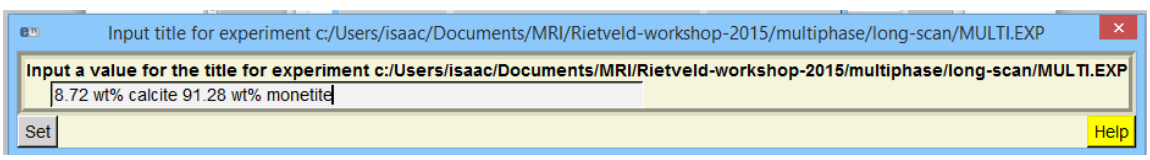
Enter a name for the experiment file e.g. multi in the box at the bottom and press **Read**



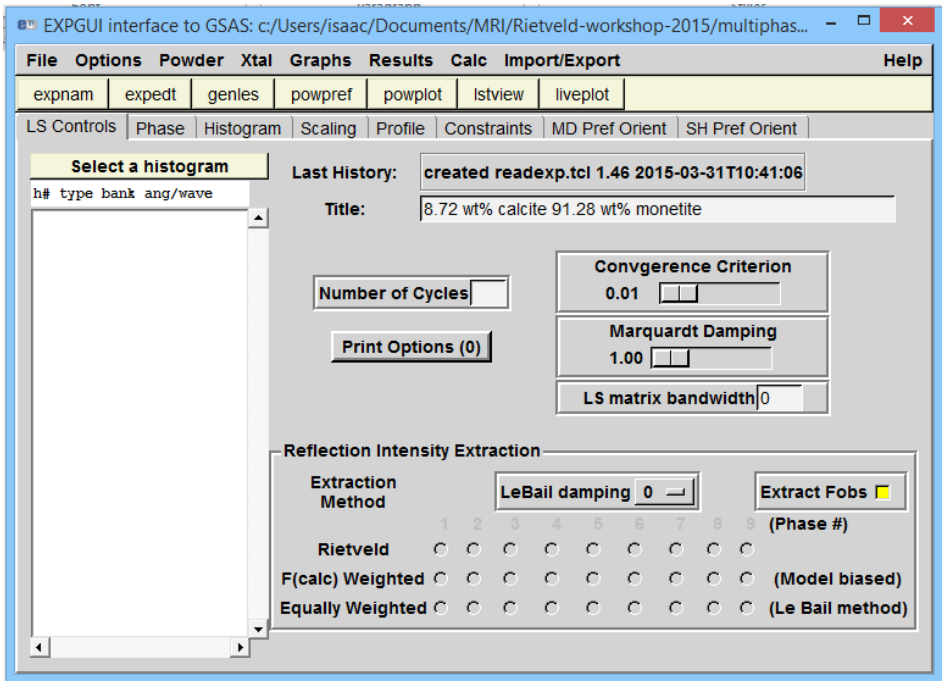
You will be prompted that the file does not exist and if you wish to create it. Press **Create**



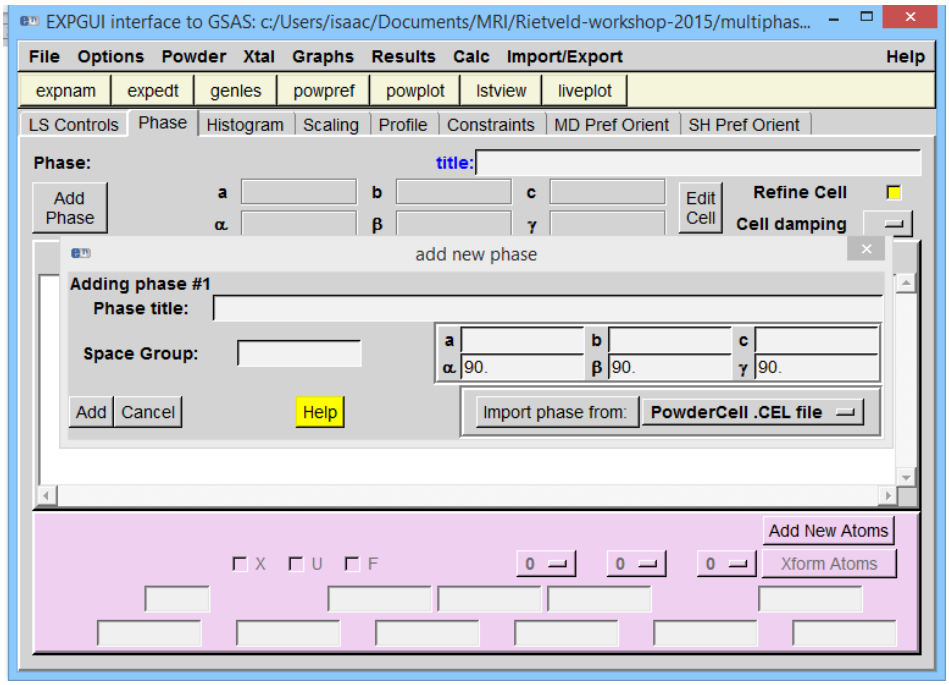
When prompted enter a suitable experiment title and press **Set**.



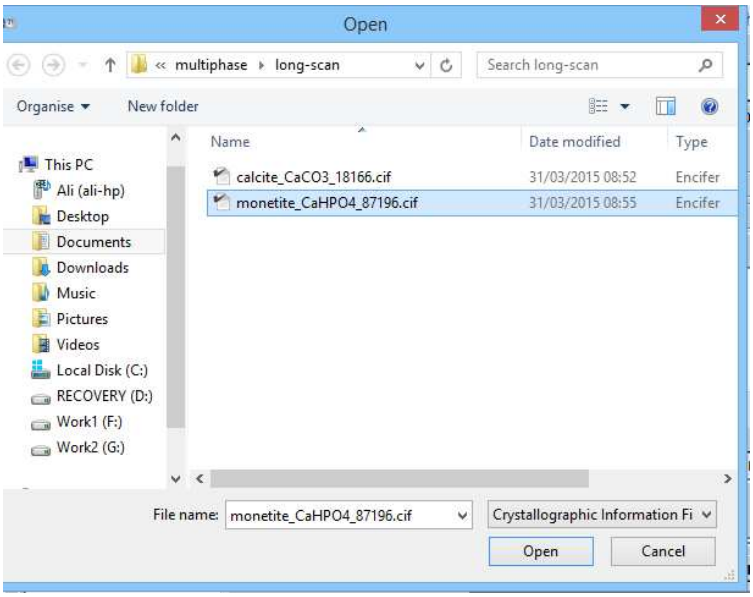
The main Expgui screen will now appear.



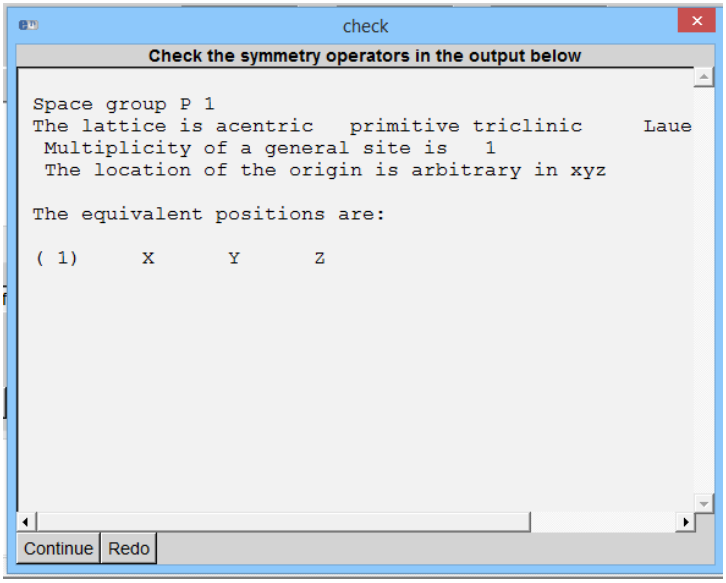
Then click on the **Phase** tab and press the **Add Phase** button



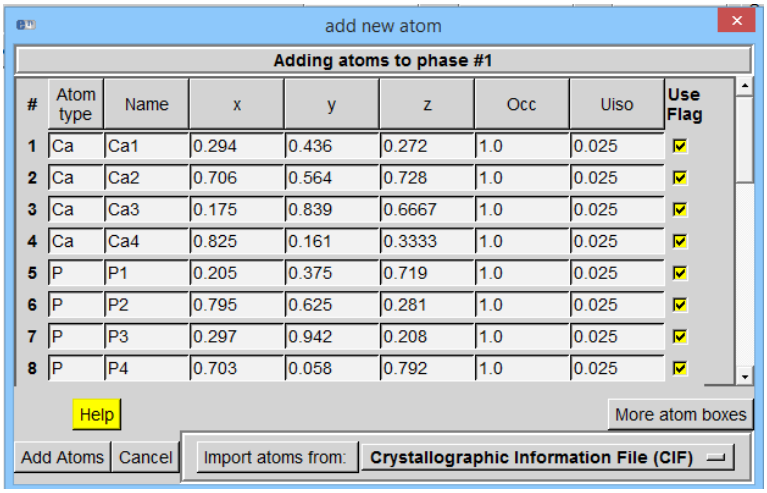
Change the file type to **Crystallographic Information File .CIF** and then press the **Import phase from:** button and read in the cif file for monetite



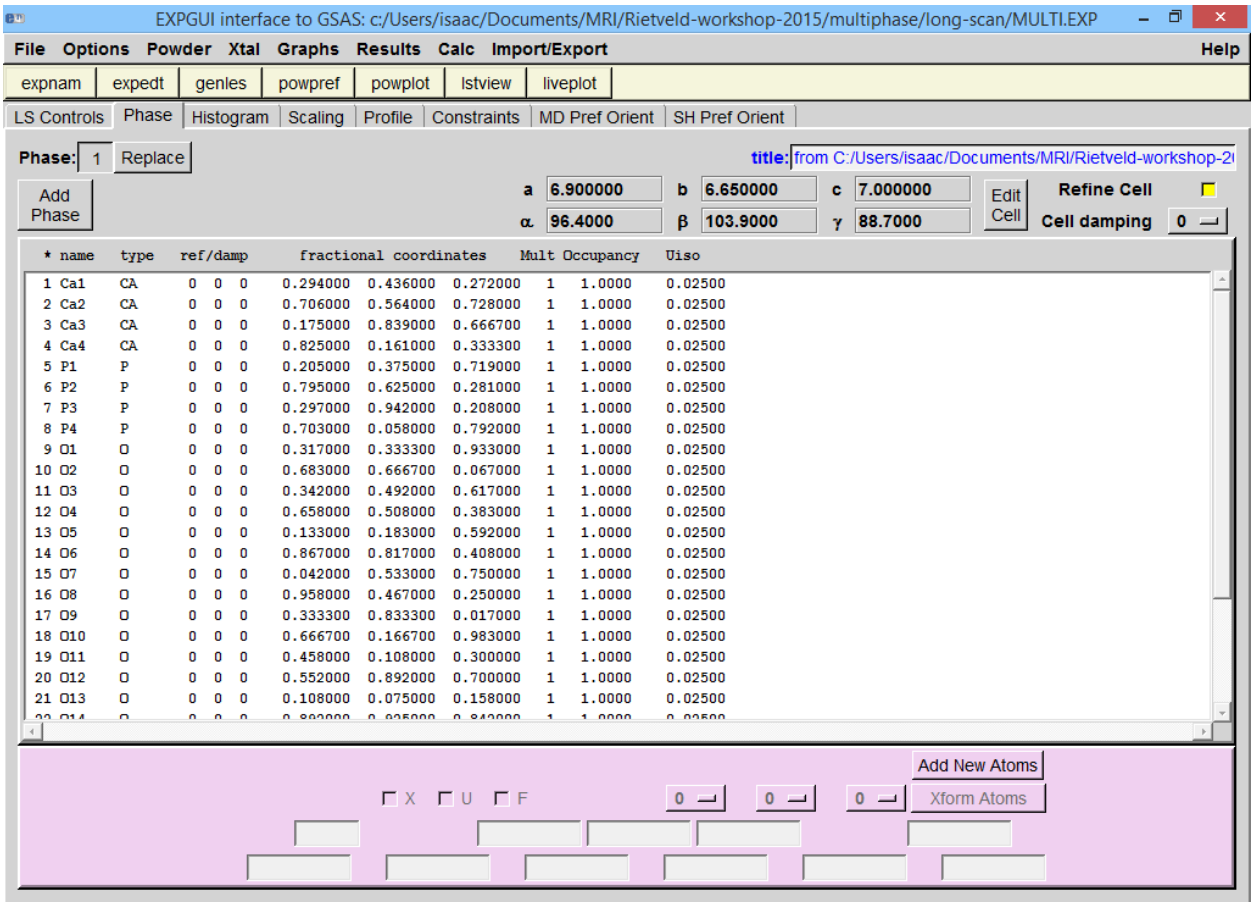
Then press the **Continue** button to open the check window



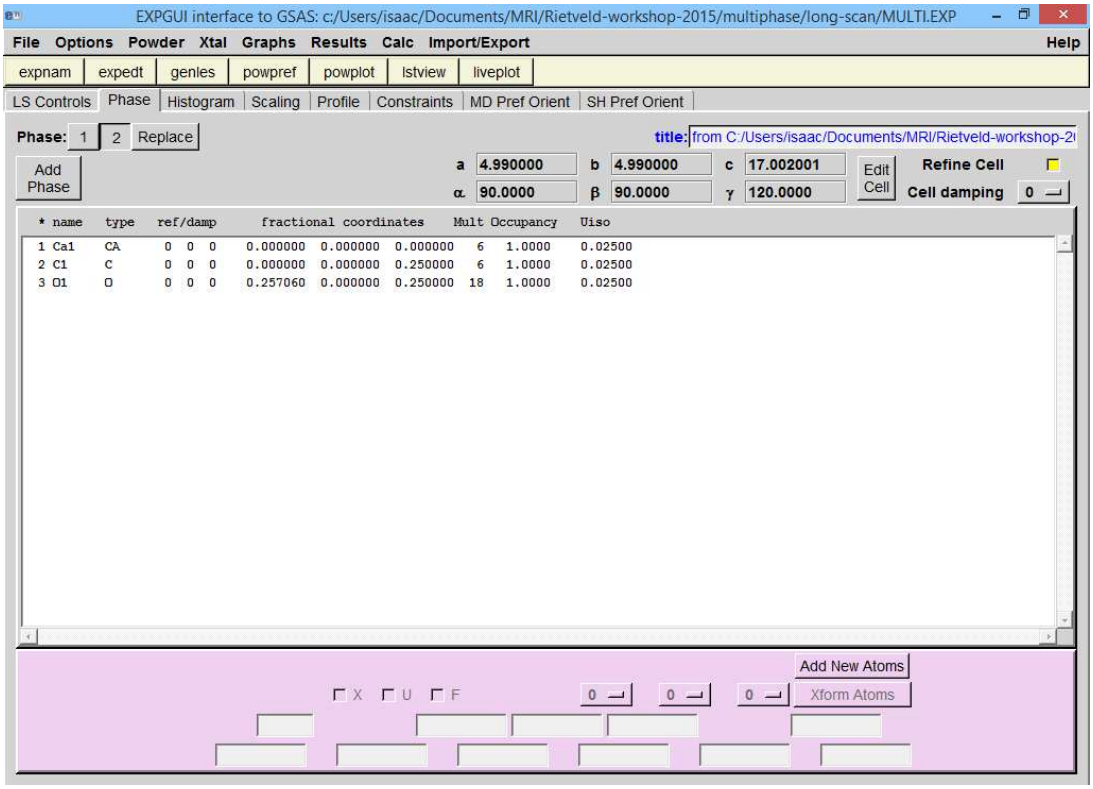
Press the **Continue** button to upload the atoms. Check the atoms have uploaded correctly and adjust as required. Typically refinement is carried out using neutral atoms rather than ions. The atom types should be adjusted to Ca, P, O and H accordingly. In the Uiso boxes enter a default value of 0.025 ($Å^2$) for each atom. The Uiso term refers to the isotropic thermal parameter.



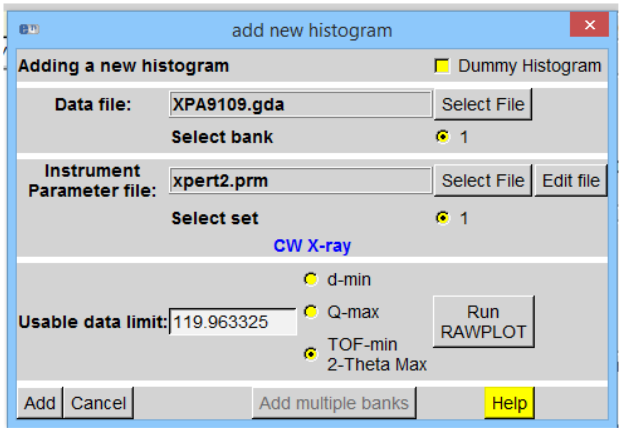
When complete press the **Add Atoms** button.



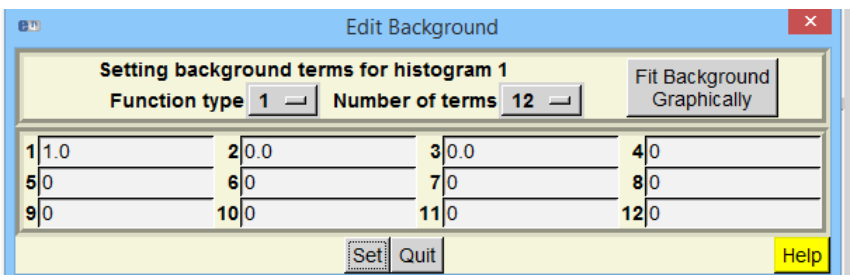
Repat the process for the calcite secondary phase. Note you will receive a warning that the space group R -3 c H is not recognised. You need to edit the space group to R -3 c



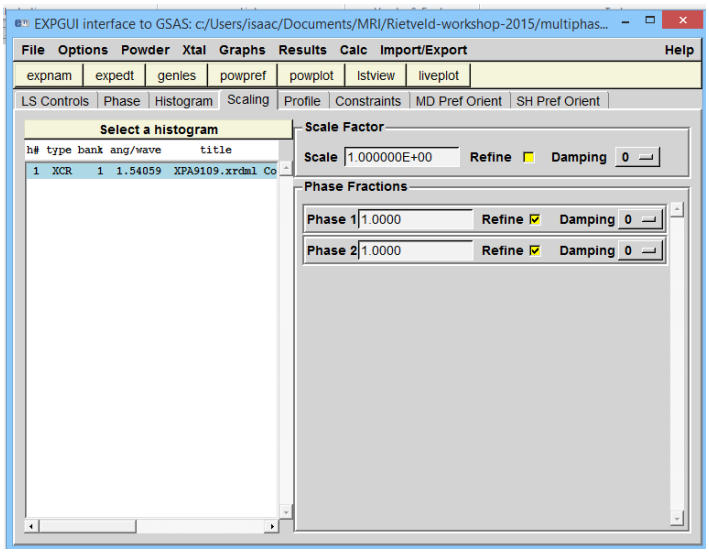
The next step is to read in the diffraction data. In GSAS these are termed as histograms. Click on the **Histogram** tab and then click on the **Add New Histogram** button. Select the data file **XPA9109.gda** and the instrument parameter file **xpert2.prm**. Then press the **Add** button to complete the histogram upload.



Tho set the background type cick on the **Edit Background** button. Change the background type to 1 (Shifted Chebyschev) and the number of parameters to 12. Set the initial values of coefficient 1 to 1 and the rest to 0. Then press the **Set** button.

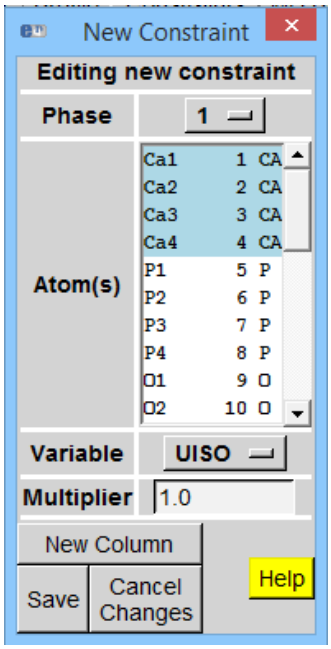


Then press the **Scaling** tab switch off refine for the **Scale Factor** and switch the **Phase Fractions** to refine.

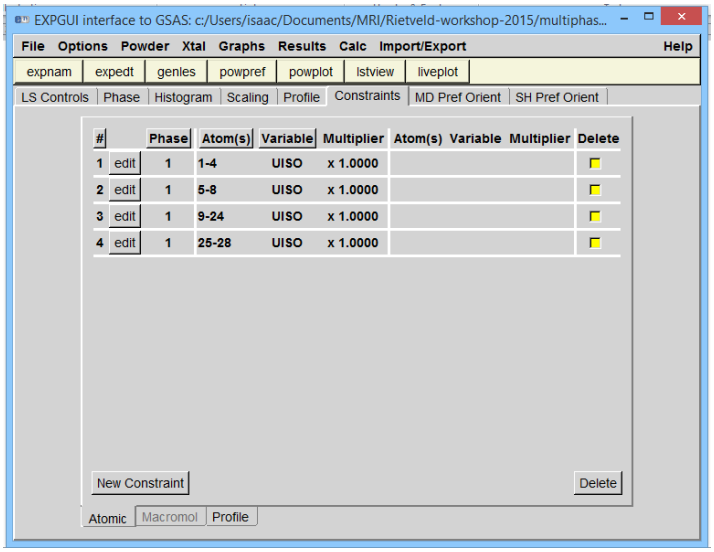


You then need to set up constraints by clicking the **Constraints** tab and then the **New Constraint** button.

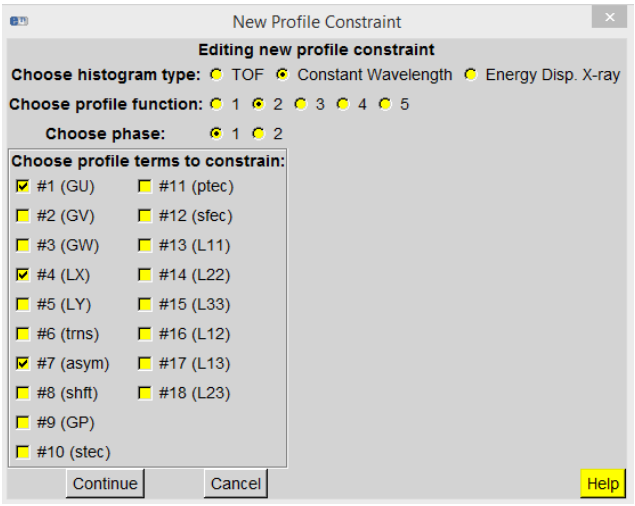
For Phase 1 set all the Ca atoms to have the same Uiso. Set the Phase to 1 the Variable to Uiso and the Multiplier to 1.0 then press **Save**



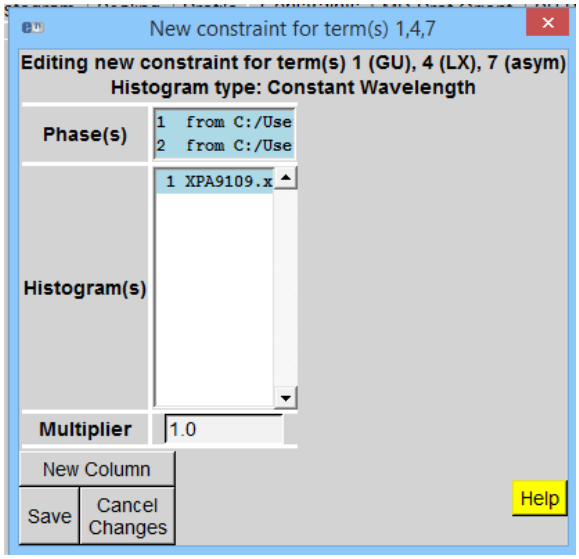
Repeat for the P, O and H atoms

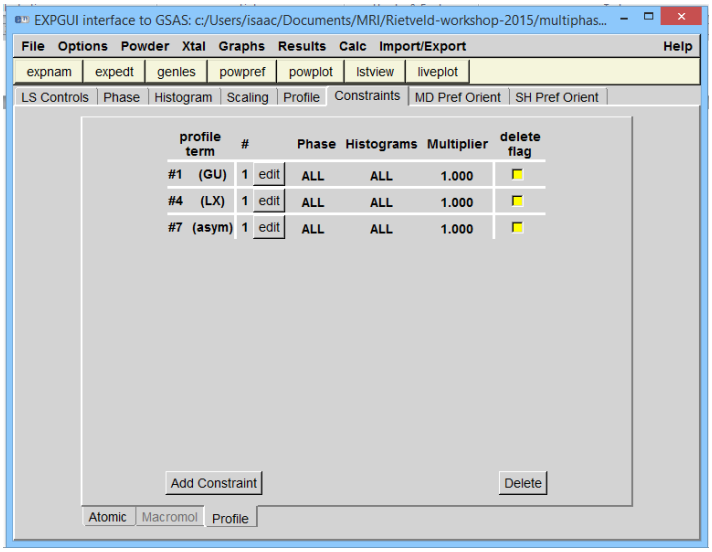


Then press the **Profile** tab at the bottom of the constraints screen and press **Add Constraint**. Then for **phase 1** click on **GU**, LX and **asym** then press **Continue**.



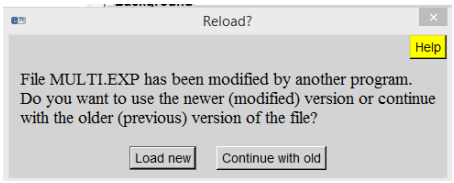
Highlight phases 1 and 2 and then **Save**



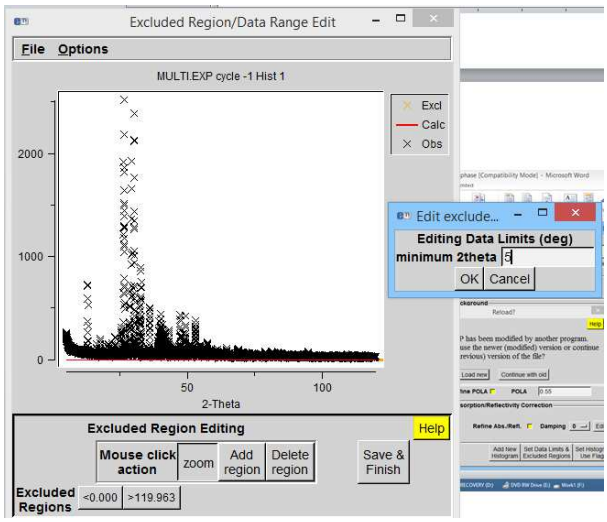


The basic set up is now complete.

The next stage is to run the powder preparation routine **Powpref** by clicking on the appropriate tab When prompted press any key to continue and agree to load the new EXP file



To set the min 2θ value press the **Set Data Limits & Excluded Regions** Button click on the lower limit button and set to 5 ° and then press **Save & Finish**



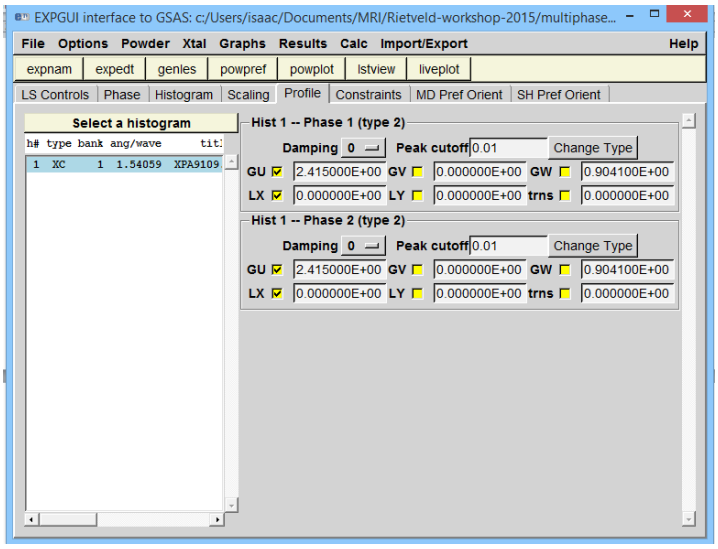
Run **Powpref** and then **Genles** by pressing on the appropriate tabs. Load the new EXP file when prompted.

You can view the success of the refinement using Liveplot (press the **Liveplot** tab)

Next refine the cell dimensions for Phase 1 under the Phase tab and run **Genles** again, repeat for phase 2

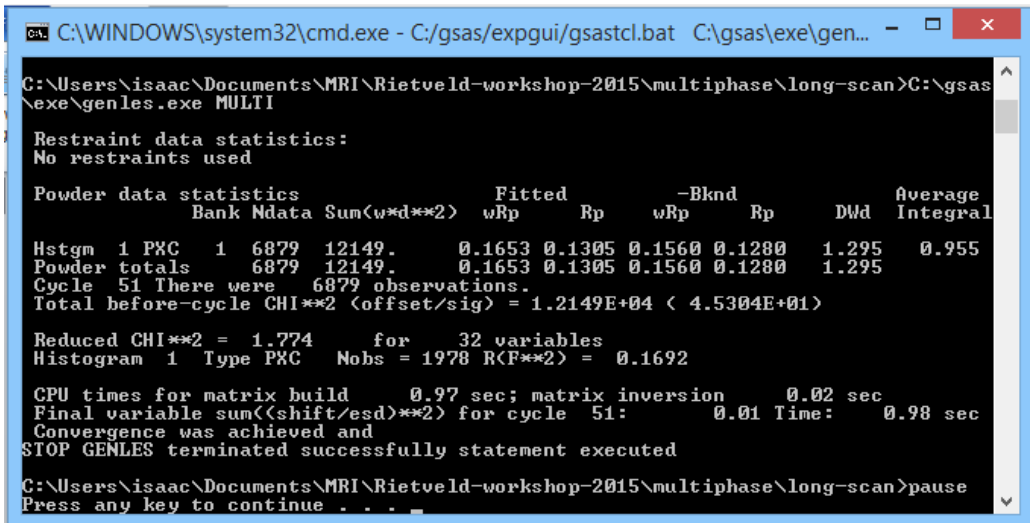
Run **Powpref** and then **Genles** again.

Next click on refine **GU** and **LX** for both phases and run **Genles** again, continue to run **Genles** until the Rwp value stays fairly constant. Then rerun Powpref and Genles once more.



Under **Histogram** now refine the **zero** point. Run Genles followed by **Powpref** and **Genles** again Next refine the Uiso values for the Ca, P and O atoms for phase 1 and the Ca C and O atoms for phase 2. Finally refine the**asymmetry** profile parameters for both phases.

Run **Genles** and **Powpref** until you are satisfied that the R-factors are at minumum values or you reach convergence.

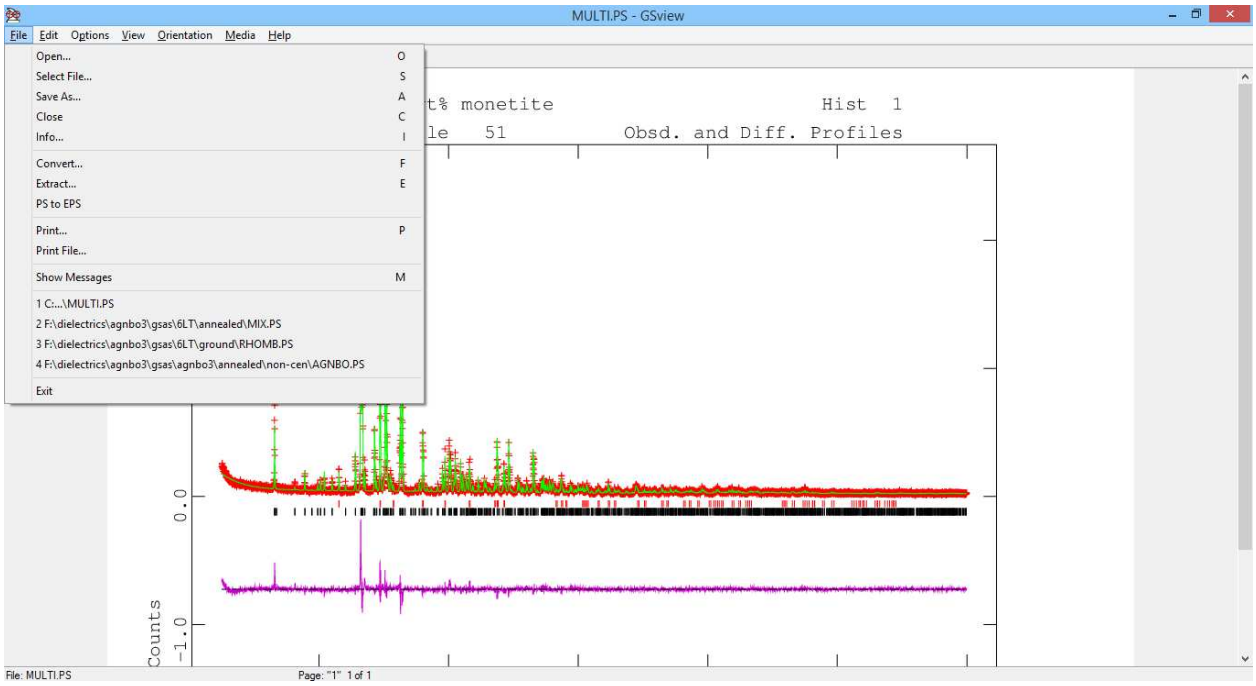


For a final plot use Powplot (press the **Powplot** tab)

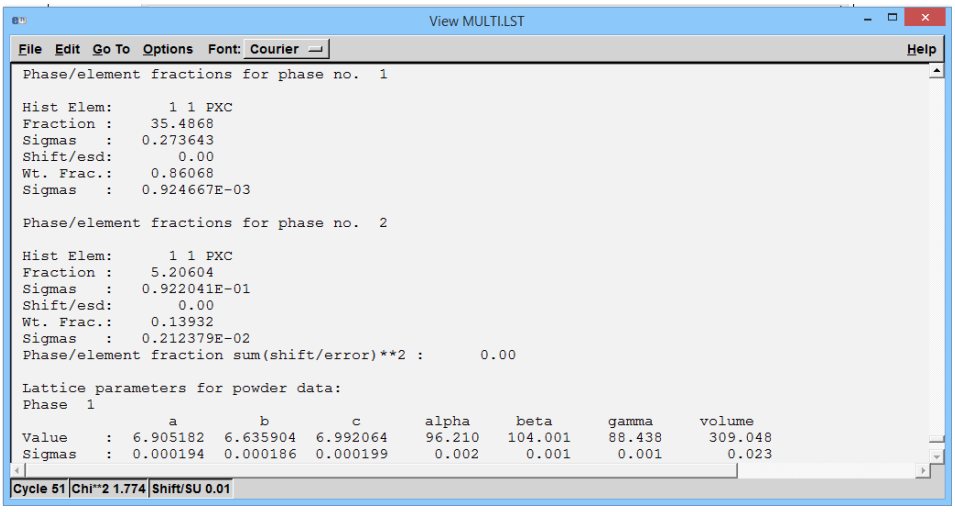
For graphic screen option use **option C**. Answer **Y** to save graphics output and **option D** to save a colour poscript file

Enter the histogram (press **H** followed by **1**)
Press **D** for a difference plot, **M** for reflection markers and **P** to plot

To switch between graphics and command prompt windows use press **ALT** and **Tab** keys together. In the command prompt window click **Y** to save a hard copy. Then press the **return** button twice and **X** to exit. To view and convert the the postscript file **GSView** and **Ghostscript** are recommended.



You can examine the phase fractions in **lstview** (Lstview tab in EXPgui) or using **notepad** to open the .lst file in Windows



In this example the weight fractions are within 0.6% of the value based on the original mixture. To improve the fit model parameters such as the atomic coordinates need to be refined.