OAK RIDGE National Laboratory

TOPAZ

GSAS/EXPGUI refinement example

Xiaoping Wang

Neutron Scattering Division

Single Crystal Neutron Diffraction Experiment

The tutorial is for locating hydrogen atoms on the water molecules in scolecite using neutron data measured on TOPAZ.

Scolecite is a member of *nat* zeolites with a porous aluminosilicate framework analogous to natrolite but a different placement of the calcium cation and water molecules in the zeolite channels.

A block-shaped crystal with the dimension of 0.62 × 1.19 × 1.63 mm-cubed was cut from a prismatic scolecite crystal originated from India, and mounted with cyanoacrylate glue on the tip of a polyamide capillary to minimize the scattering from the mount. The initial orientation matrix was obtained in ISAWEV at 100 K. Using this orientation matrix, an optimized data collection strategy was calculated in CrystalPlan [1]. Data were collected using 39 crystal orientations for an estimated 99.7% coverage of symmetry-equivalent reflections to d_{min} of 0.5 Å. An estimated 90% of the measured reflections would be measured more than once. Each orientation was measured for approximately 1.5 h.

Scolecite	$CaAl_2Si_3O_{10}\cdot 3H_2O$
Temperature	100(2) K
Radiation source	TOF neutron
wavelengths	0.4 – 3.2 Å
Crystal system	Monoclinic
Space group	C c
***a*, Å**	6.5120(1)
***b*, Å**	18.9545(4)
***c*, Å**	9.7582(2)
***β*, °**	108.921(1)
V, Å³	1139.39(4)
Z	4

[1] Zikovsky J., Peterson P. F., Wang X. P., Frost M., Hoffmann C., "CrystalPlan: an experiment-planning tool for crystallography", ", *J. Appl. Cryst.* **44**, 418-423 (2011)

Scolecite Data

- Single crystal diffraction data are saved in /SNS/TOPAZ/IPTS-12132/data
  - Event NeXus

    TOPAZ_#####_event.nxs
- **100 K Data Set**
  - Run numbers 7450:7488
- **295 K Data Set**
  - Run numbers 10074:10079,10081:10084

Start EXPGUI

- Copy the hkl data *scolecite100K_Monoclinic_C.hkl* to GSAS folder

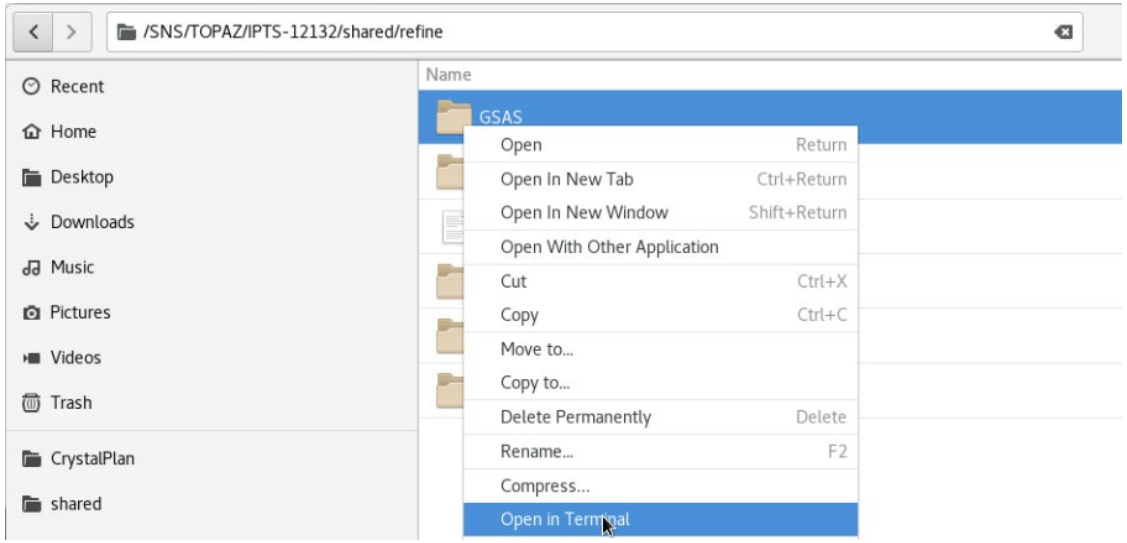
  from /SNS/TOPAZ/IPTS-12132/shared/SC100K/

  to the working directory /SNS/TOPAZ/IPTS-12132/shared/refine/GSAS/

Open a terminal window in /SNS/TOPAZ/IPTS-12132/shared/refine/GSAS [as shown below]

- Type ls *.hkl to verify the hkl data is available
- Execute **expgui** in terminal window

  to start the GSAS program
- Start EXPGUI by typing expgui

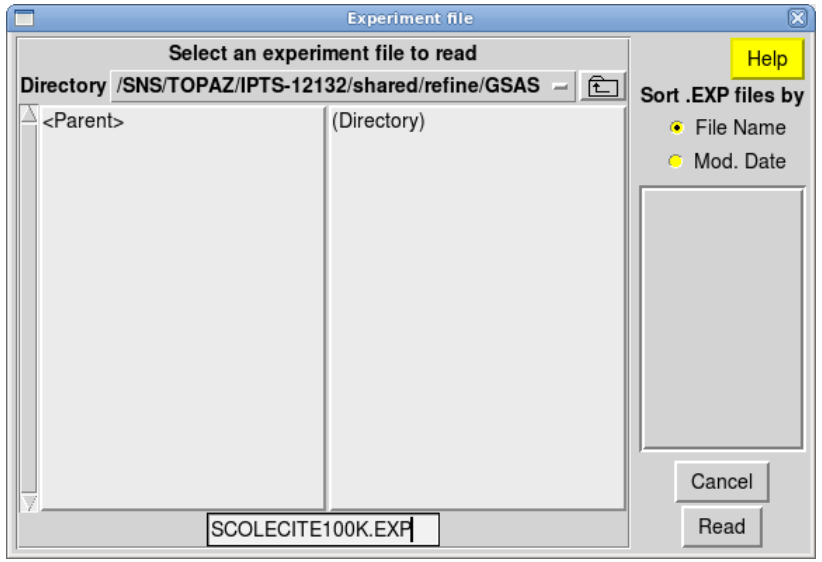


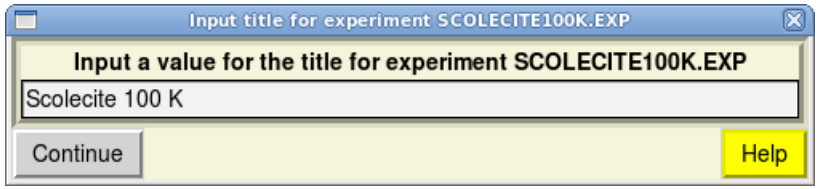
$ expgui

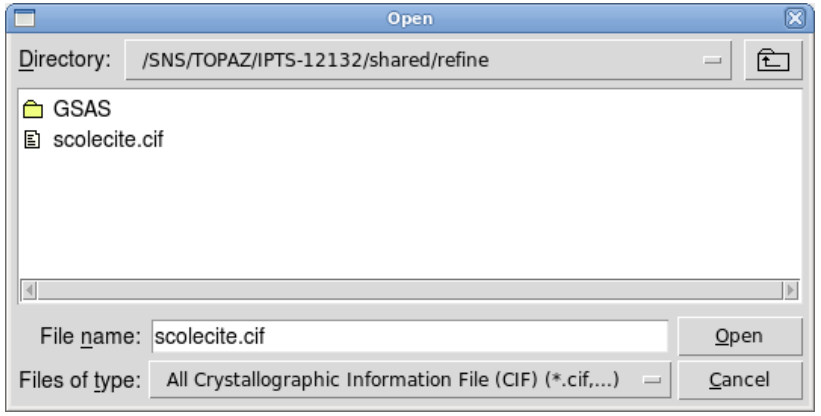
Create GSAS EXP

- Type in SCOLECITE100K.EXP
- Click Read
- Click Create
- Input Soclecite 100 K
- Click Continue
- Click Add Phase
- Select scolecite.cif from

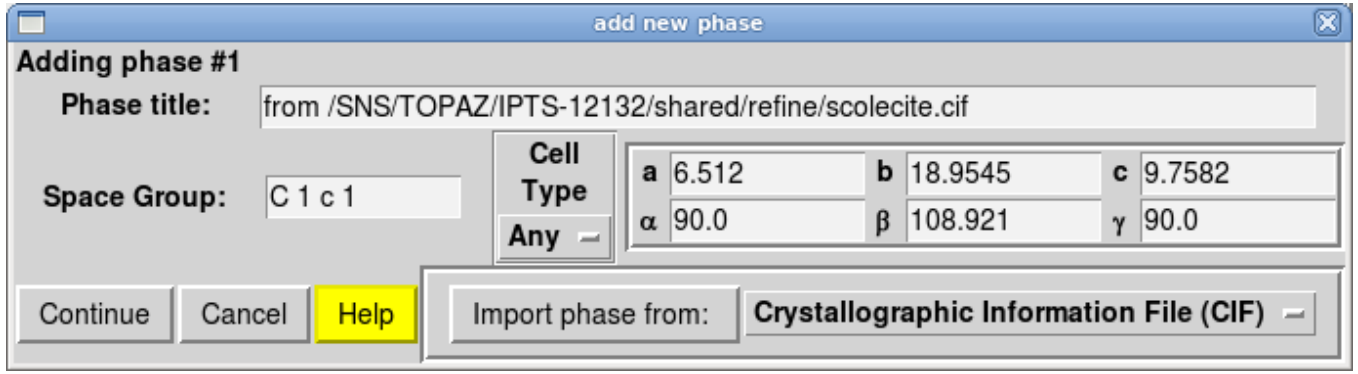
  /SNS/TOPAZ/IPTS-12132/shared/refine

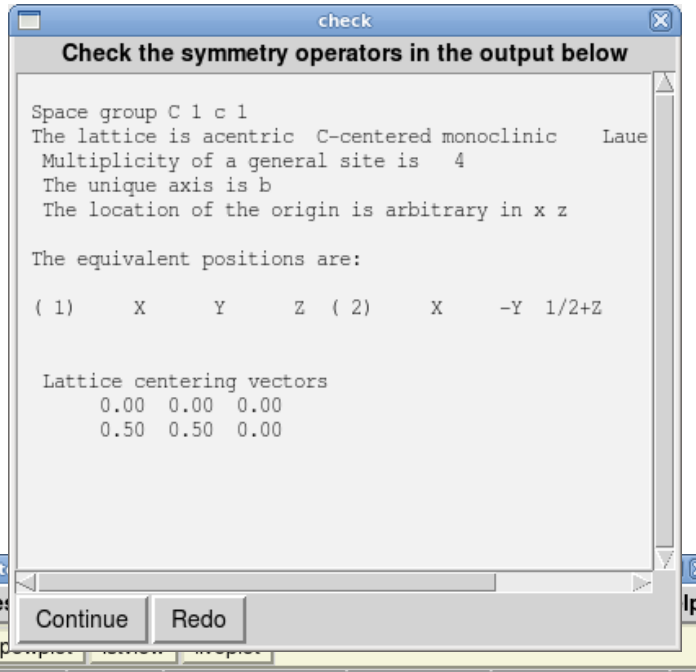


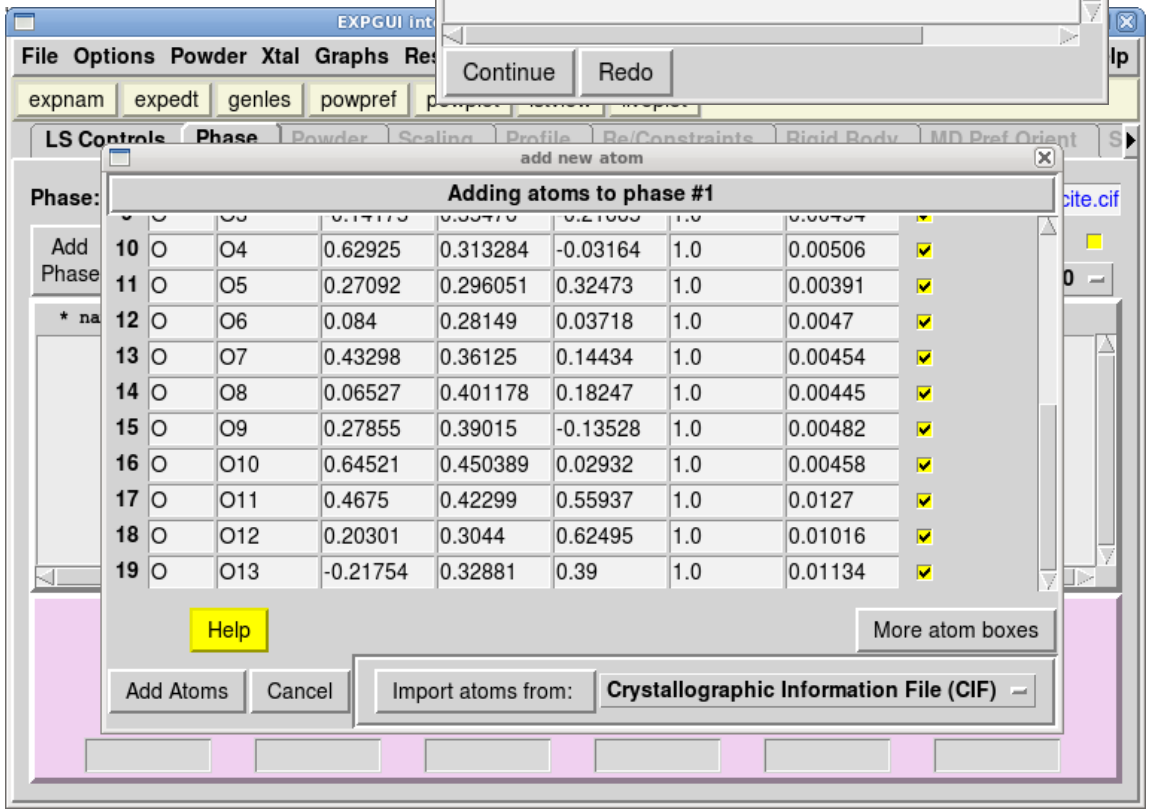




Import scolecite cif

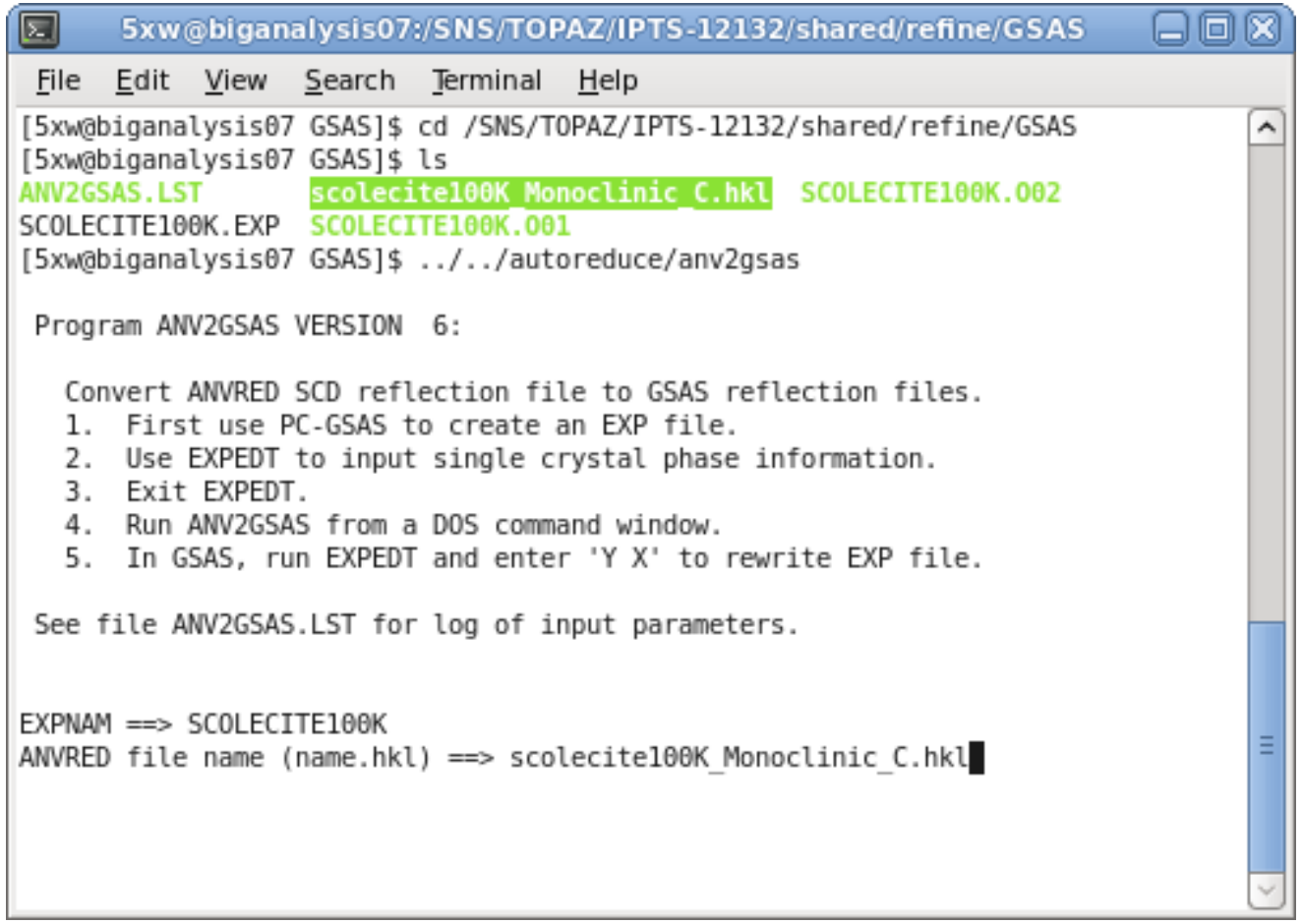




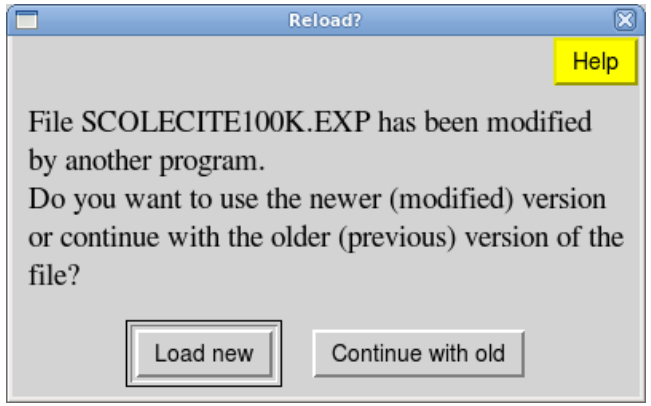


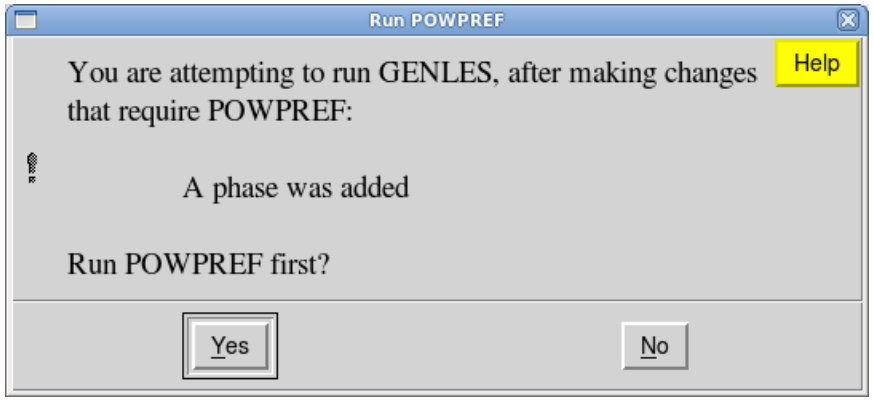
- Save SCOLECITE100K.EXP
- Click File
  Save

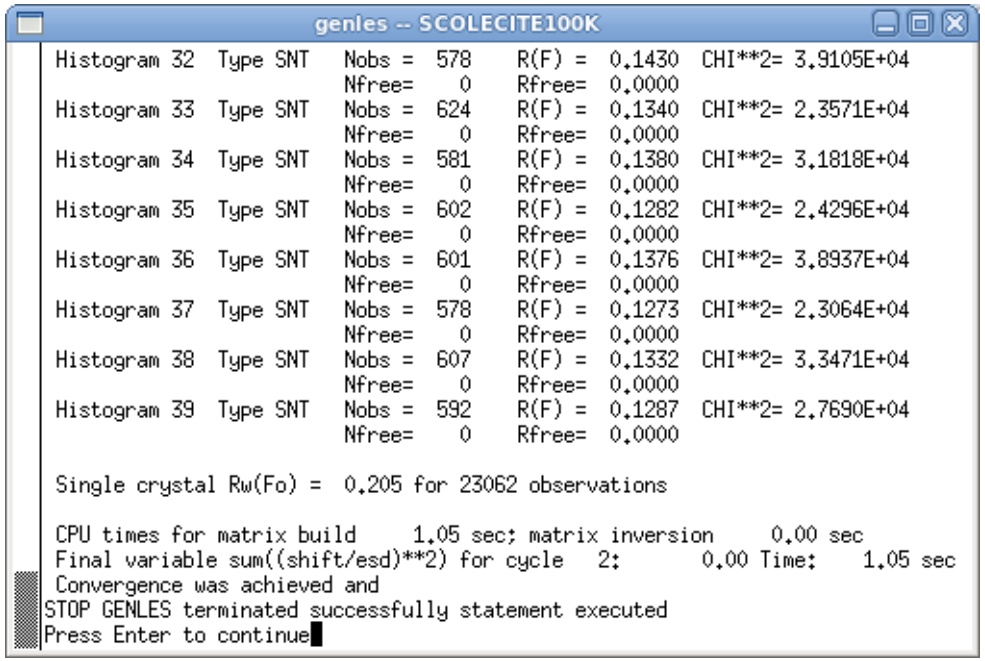
Convert TOPAZ Data to GSAS Format



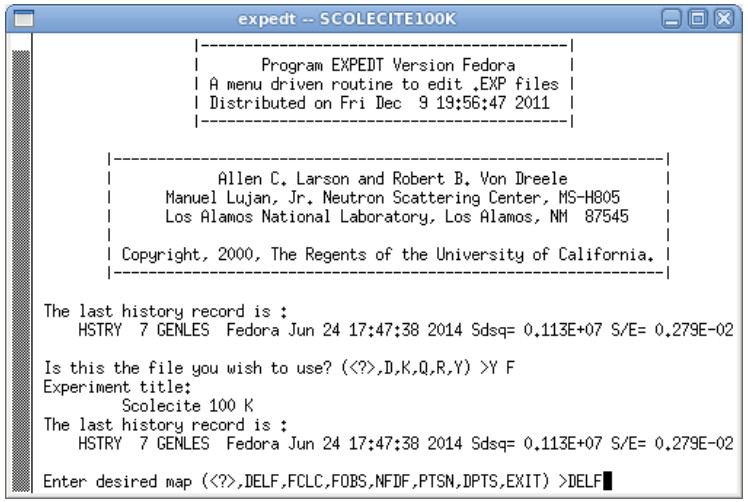
Run Genles


Reload?
Help
File SCOLECITE100K.EXP has been modified by another program.
Do you want to use the newer (modified) version or continue with the older (previous) version of the file?
Load new
Continue with old


Run POWPREF
Help
You are attempting to run GENLES, after making changes that require POWPREF:
A phase was added
Run POWPREF first?
Yes
No


genles -- SCOLECITE100K
Histogram 32 Type SNT Nobs = 578 R(F) = 0.1430 CHI**2= 3.9105E+04
Nfree= 0 Rfree= 0.0000
Histogram 33 Type SNT Nobs = 624 R(F) = 0.1340 CHI**2= 2.3571E+04
Nfree= 0 Rfree= 0.0000
Histogram 34 Type SNT Nobs = 581 R(F) = 0.1380 CHI**2= 3.1818E+04
Nfree= 0 Rfree= 0.0000
Histogram 35 Type SNT Nobs = 602 R(F) = 0.1282 CHI**2= 2.4296E+04
Nfree= 0 Rfree= 0.0000
Histogram 36 Type SNT Nobs = 601 R(F) = 0.1376 CHI**2= 3.8937E+04
Nfree= 0 Rfree= 0.0000
Histogram 37 Type SNT Nobs = 578 R(F) = 0.1273 CHI**2= 2.3064E+04
Nfree= 0 Rfree= 0.0000
Histogram 38 Type SNT Nobs = 607 R(F) = 0.1332 CHI**2= 3.3471E+04
Nfree= 0 Rfree= 0.0000
Histogram 39 Type SNT Nobs = 592 R(F) = 0.1287 CHI**2= 2.7690E+04
Nfree= 0 Rfree= 0.0000
Single crystal Rw(Fo) = 0.205 for 23062 observations
CPU times for matrix build 1.05 sec; matrix inversion 0.00 sec
Final variable sum((shift/esd)**2) for cycle 2: 0.00 Time: 1.05 sec
Convergence was achieved and
STOP GENLES terminated successfully statement executed
Press Enter to continue

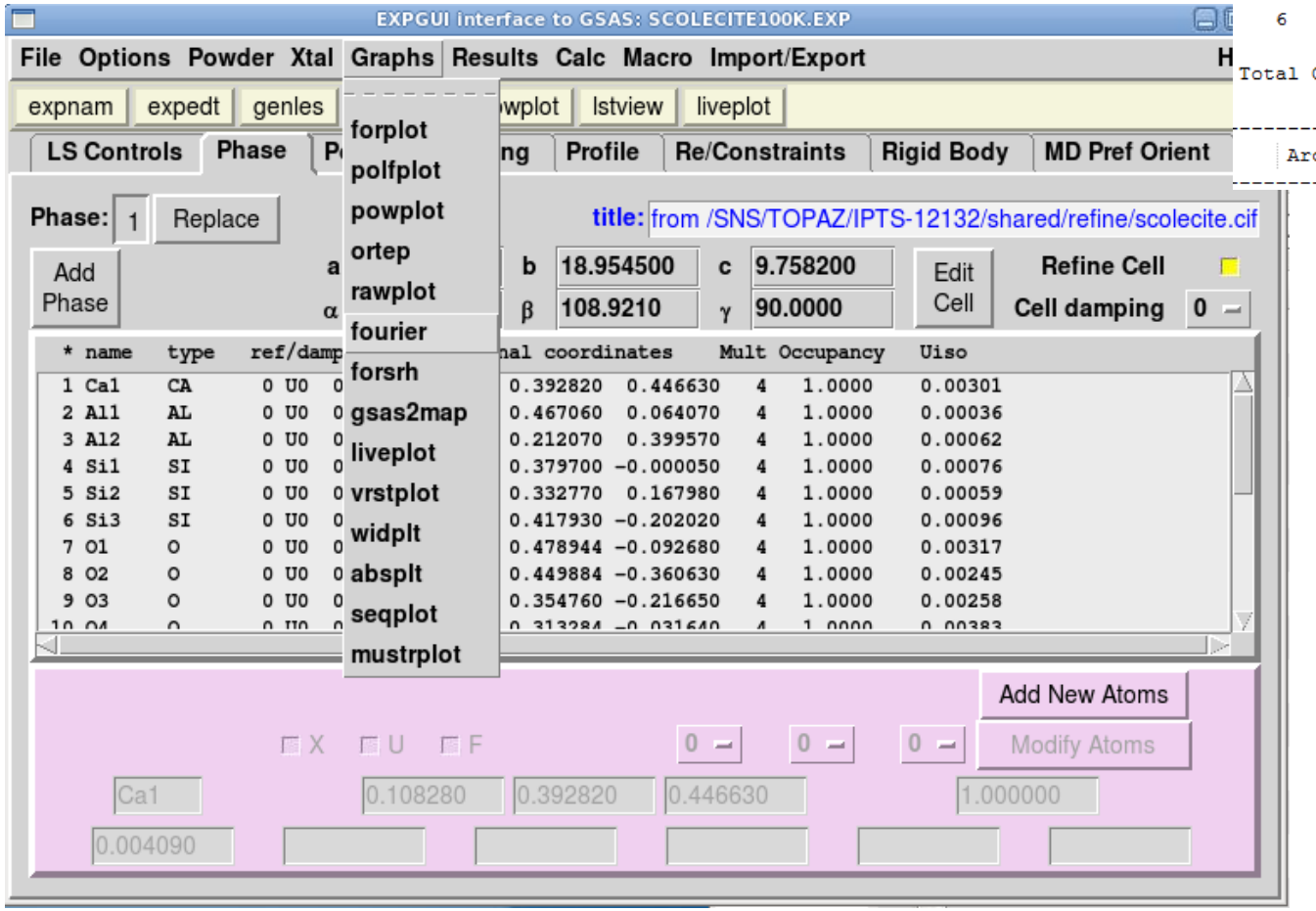
EXPEDT Difference Map Setup




```
The last history record is :
    HSTRY  9 EXPEDT  Fedora Jun 24 17:52:02 2014 File cleanup only
Is this the file you wish to use? (<?>,D,K,Q,R,Y) >Y F
Experiment title:
         Scolecite 100 K
The last history record is :
    HSTRY  9 EXPEDT  Fedora Jun 24 17:52:02 2014 File cleanup only
Enter desired map (<?>,DELF,FCLC,FOBS,NFDF,PTSN,DPTS,EXIT) >DELF
Enter section desired (X,Y,Z - choose Z for DSN6 maps) >Z
Do you wish to specify individual map steps for each axis (Y/<N>)? >Y
The a-axis is   6.512000 A
Current del-x is  0.2000 A
Enter Fourier calculation spacing in Angstroms along the a-axis >0.1
The new del-x is  0.1018 A
The cell will be divided into   64 points along x
The b-axis is  18.954500 A
Current del-y is  0.2000 A
Enter Fourier calculation spacing in Angstroms along the b-axis >0.1
The new del-y is  0.0987 A
The cell will be divided into  192 points along y
The c-axis is   9.758200 A
Current del-z is  0.2000 A
Enter Fourier calculation spacing in Angstroms along the c-axis >0.1
The new del-z is  0.0976 A
The cell will be divided into  100 points along z
Old x limits are  0.0000 to  0.0000
Enter minimum and maximum values of x in fractions of the cell edge >0 1
New x limits are  0.0000 to  1.0000
Old y limits are  0.0000 to  0.0000
Enter minimum and maximum values of y in fractions of the cell edge >0 1
New y limits are  0.0000 to  1.0000
Old z limits are  0.0000 to  0.0000
Enter minimum and maximum values of z in fractions of the cell edge >0 1
New z limits are  0.0000 to  1.0000
At least one asymmetric part of the unit cell is included in the Fourier.
Enter new list of histogram numbers in the order you wish them to be read.
The last occurrence of a reflection will be used.
Include histogram (0 to terminate list) >1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 0
Enter FOURIER map option (<?>,A,C,D,E,F,H,I,L,P,R,S,T,W,X) >
```

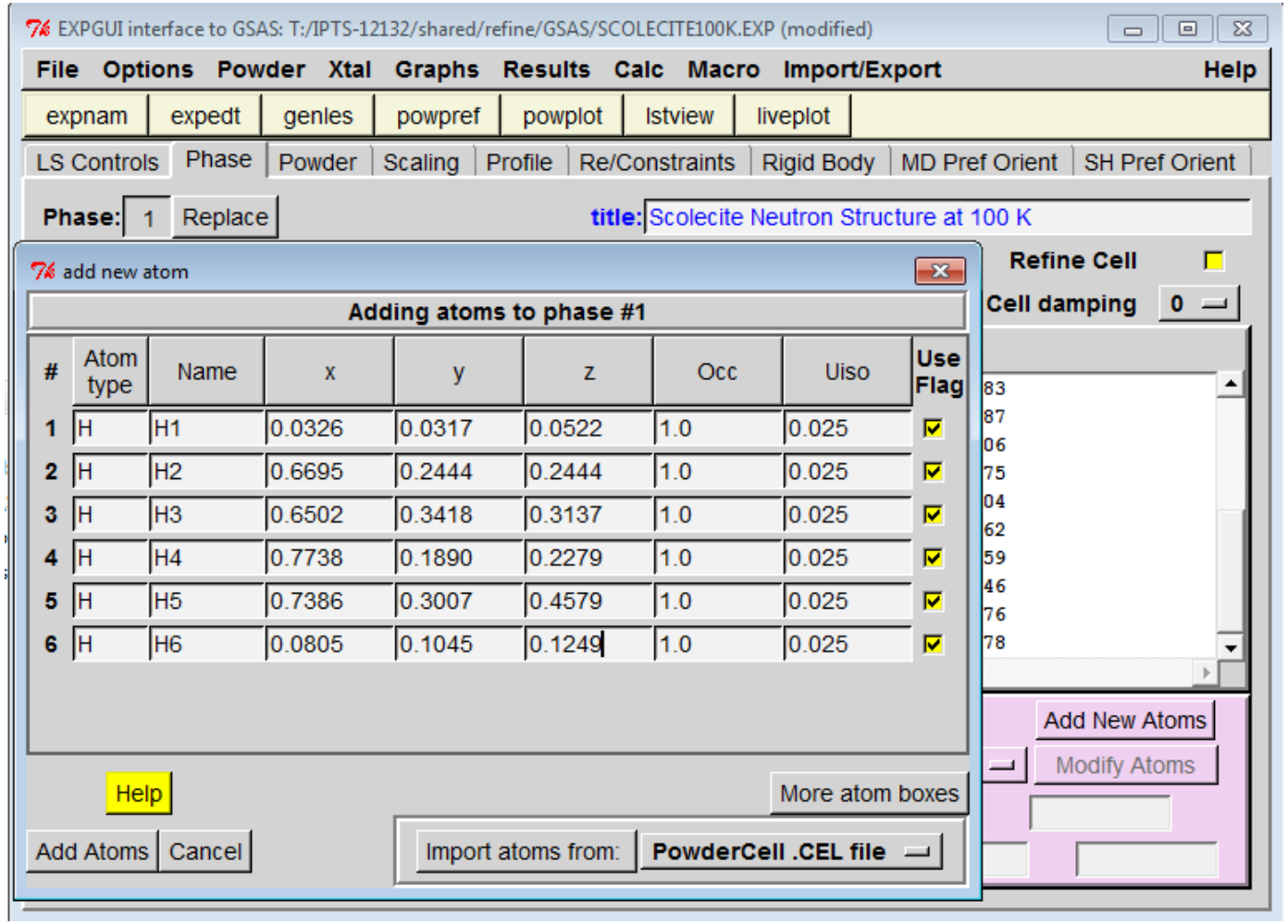
Search for Hydrogen

- Run fourier
- Run forsrh



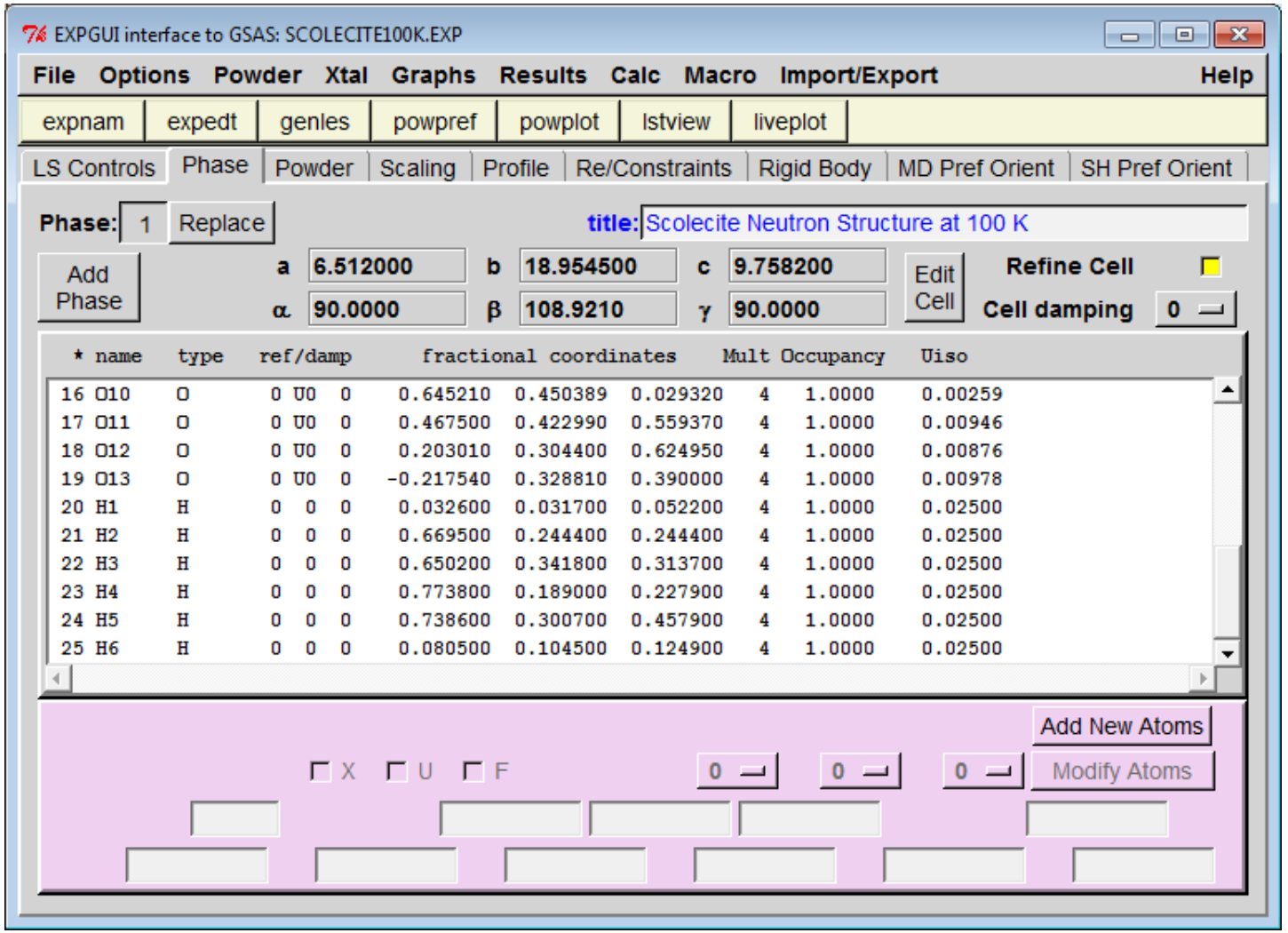

```
Min rho =   -1.00000  No. of peaks =  10  Peaks saved? N

Phase I.D. from /SNS/TOPAZ/IPTS-12132/shared/refine/scolecite.cif
Data  I.D. Scolecite 100 K
Map type is DELF

The following peaks were found
          Rho       X       Y       Z
   1     -2.283  0.0326  0.0317  0.0522
   2     -2.176  0.6695  0.2444  0.0977
   3     -2.009  0.6502  0.3418  0.3137
   4     -1.986  0.7738  0.1890  0.2279
   5     -1.910  0.7386  0.3007  0.4579
   6     -1.845  0.0805  0.1045  0.1249

Total CPU time for FORSRH was   0.09 seconds

-------------------------------------------
   Archiving SCOLECITE100K.EXP as SCOLECITE100K.00A
-------------------------------------------
```

Add Hydrogen from DELF Map Output



Refine Histogram Scale Factors

Rw(Fo) = 0.117



Refine Extinction

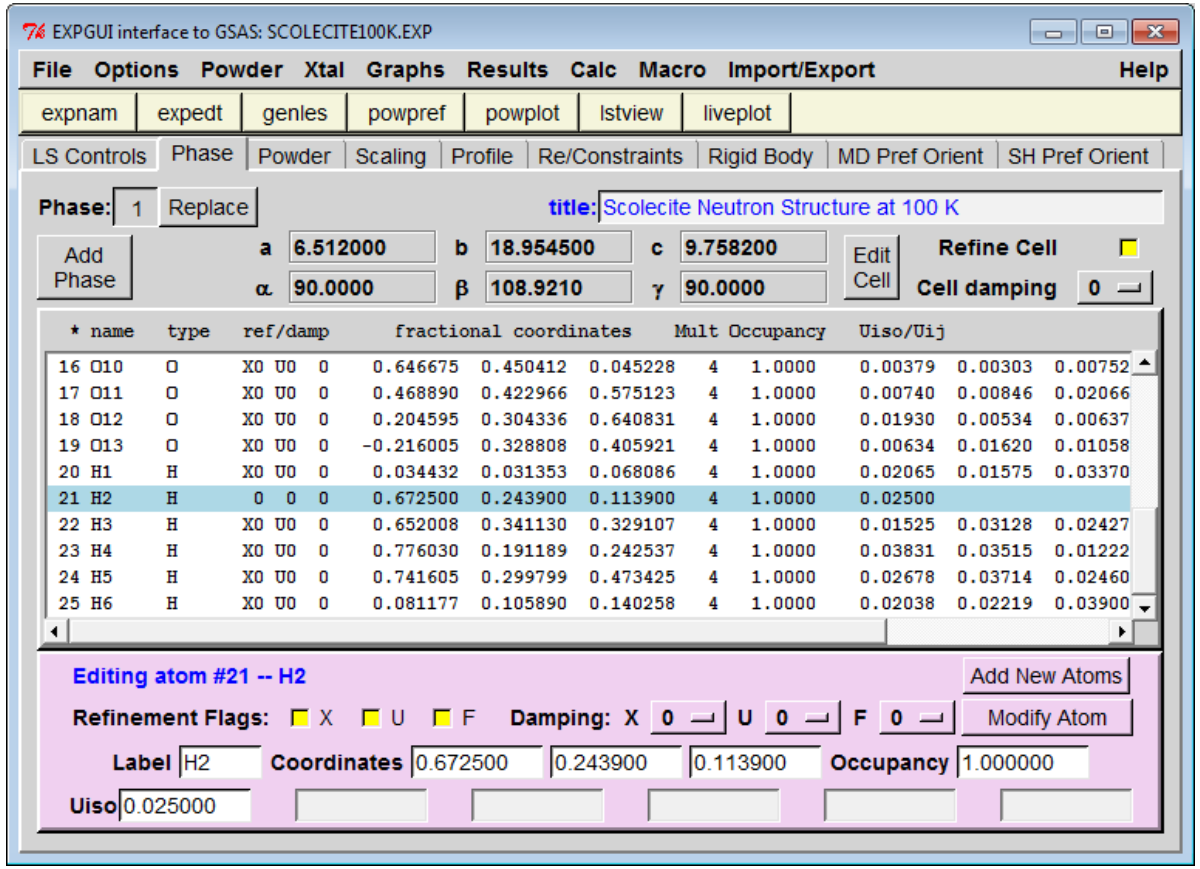
```
Editing single crystal extinction parameters:

Phase no. 1
Title: from /SNS/TOPAZ/IPTS-12132/shared/refine/scolecite.cif
Extinction for crystal element no.  1:
Current extinction type:
Secondary Type-I     Value = 1.0000E-10 Refine(N)  Damp flag = 0
Lorentzian model used
Single crystal extinction editing option? (<?>,C,D,L,T,V,X) >T
Select new extinction type:
Enter extinction type flag, (<?>,0-4) >1
Do you want to use the Lorentzian model (Y/<N>)? >Y
Current extinction type:
Secondary Type-I     Value = 1.0000E-10 Refine(N)  Damp flag = 0
Lorentzian model used
Single crystal extinction editing option? (<?>,C,D,L,T,V,X) >V
The Type-I   refinment flag was changed to Y
Current extinction type:
Secondary Type-I     Value = 1.0000E-10 Refine(Y)  Damp flag = 0
Lorentzian model used
Single crystal extinction editing option? (<?>,C,D,L,T,V,X) >X
Enter overall parameter to be edited (<?>,E,H,S,T,X) >X
Select editing option for Least Squares calculation
 (<?>,A,B,F,H,L,O,R,S,T,X) >X
```

Search for Missing Hydrogen

- Set Occupancy to 0.0 for H2
- Run fourier
- Run forsrh

Rw(Fo) = 0.047 for 23062 observations

```
Min rho =   -1.00000  No. of peaks =  10  Peaks saved? N

Phase I.D. Scolecite Neutron Structure at 100 K
Data  I.D. Scolecite 100 K
Map type is DELF

The following peaks were found
          Rho       X       Y       Z
    1    -1.860  0.6725  0.2439  0.1139

Total CPU time for FORSRH was   0.09 seconds

------------------------------------------------
    Archiving SCOLECITE100K.EXP as SCOLECITE100K.018
------------------------------------------------
```



Extinction Coieficient and Final *R* Factors

Single crystal extinction coefficients for element 1 of phase 1 are:

Parm. : Type-I

Value : 1.286E-04

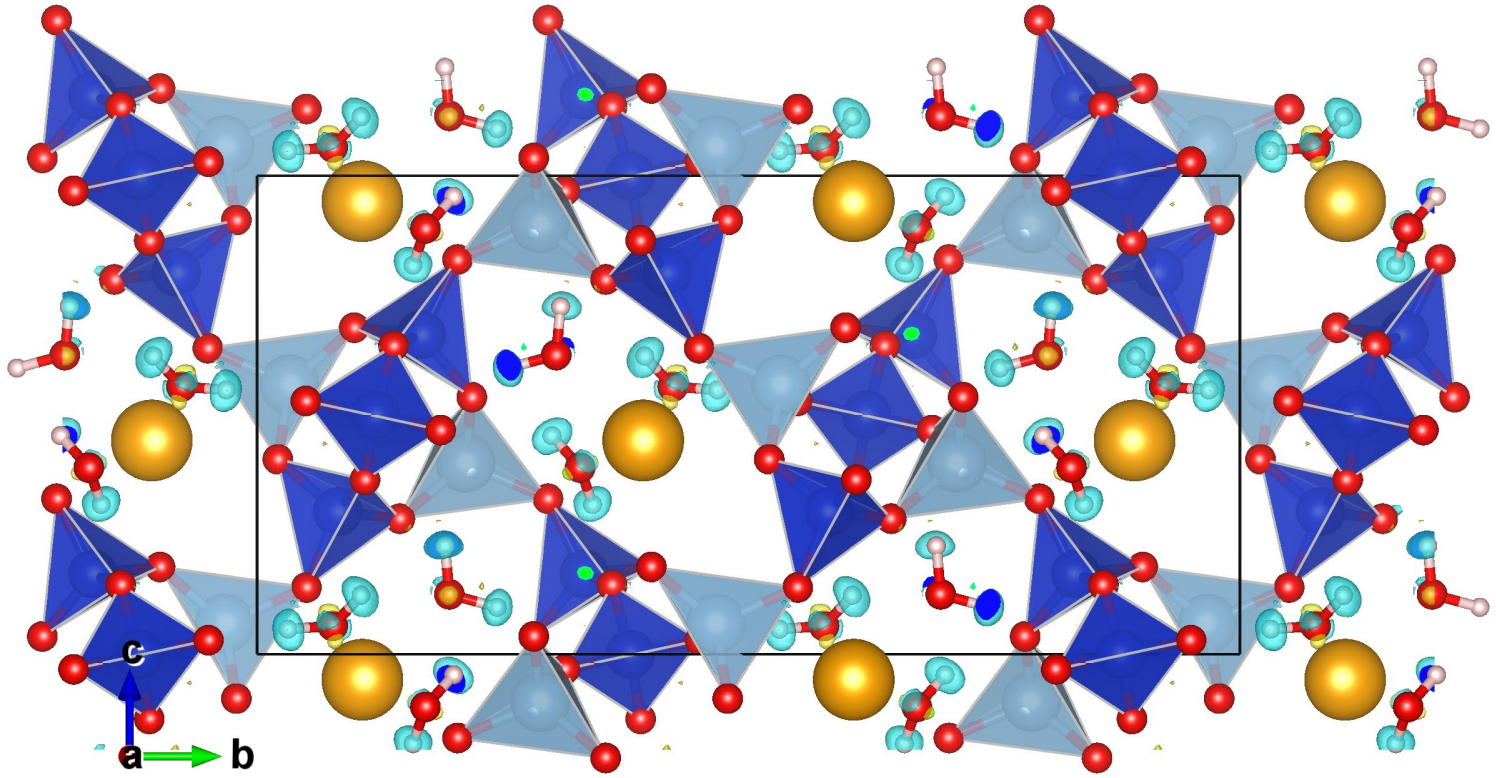
E.s.d. : 1.290E-06

Shft/esd : 0.01

Sum single crystal extinction (shift/error)**2 : 0.00

	All data		I>0.0	I>3*sigI
NREFL=	22823	22823	22303	
Rw(F**2)	0.076	0.076	0.076	
R(F**2)	0.074	0.074	0.074	
Rw(F)	-----	0.038	0.038	
R(F)	-----	0.043	0.042	

DELF Map Generated from GSAS

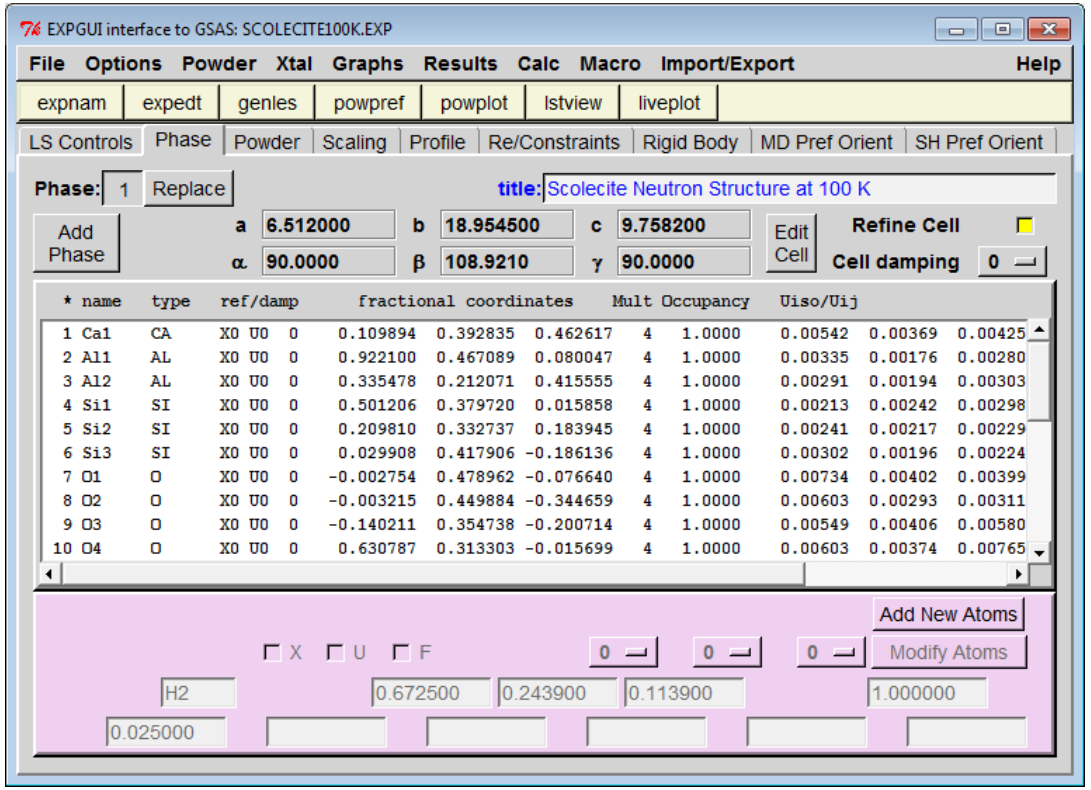


Refine ADPs for All atoms

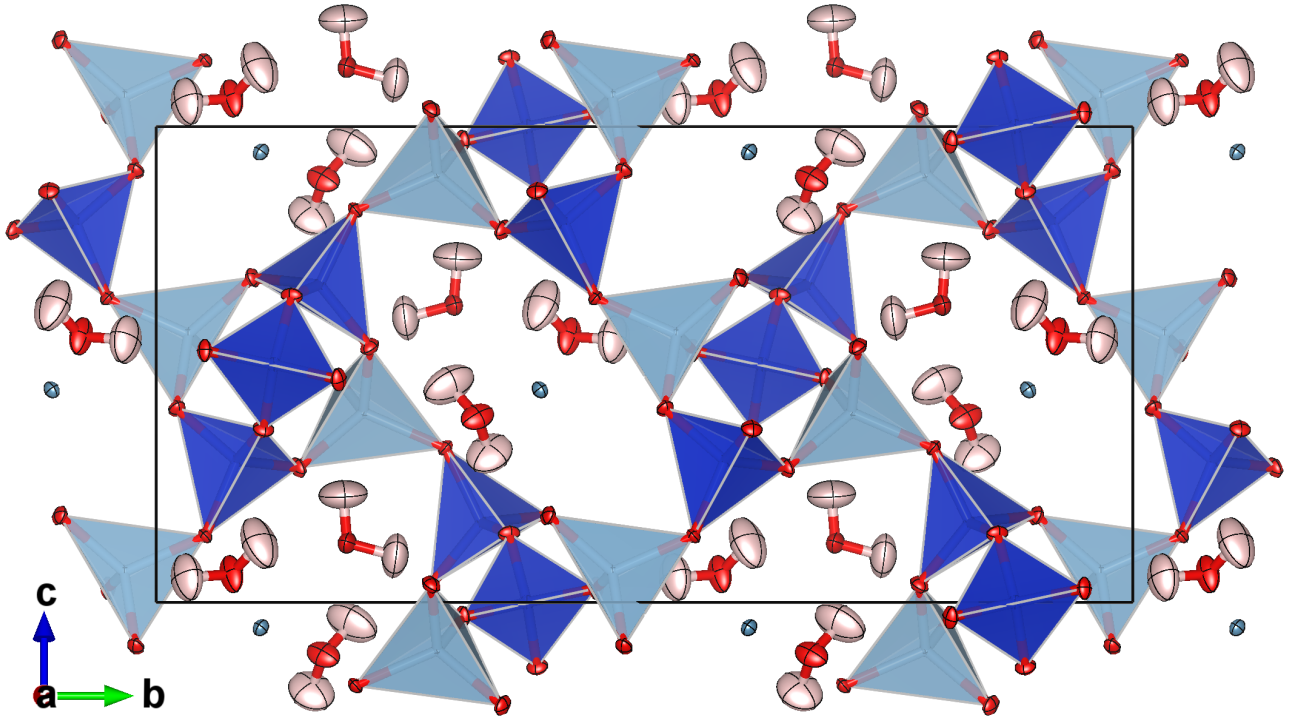
Rw(Fo) = 0.046 for 23062 observations

Rw(Fo) = 0.038 for 22823 observations
With 5σ cut-off

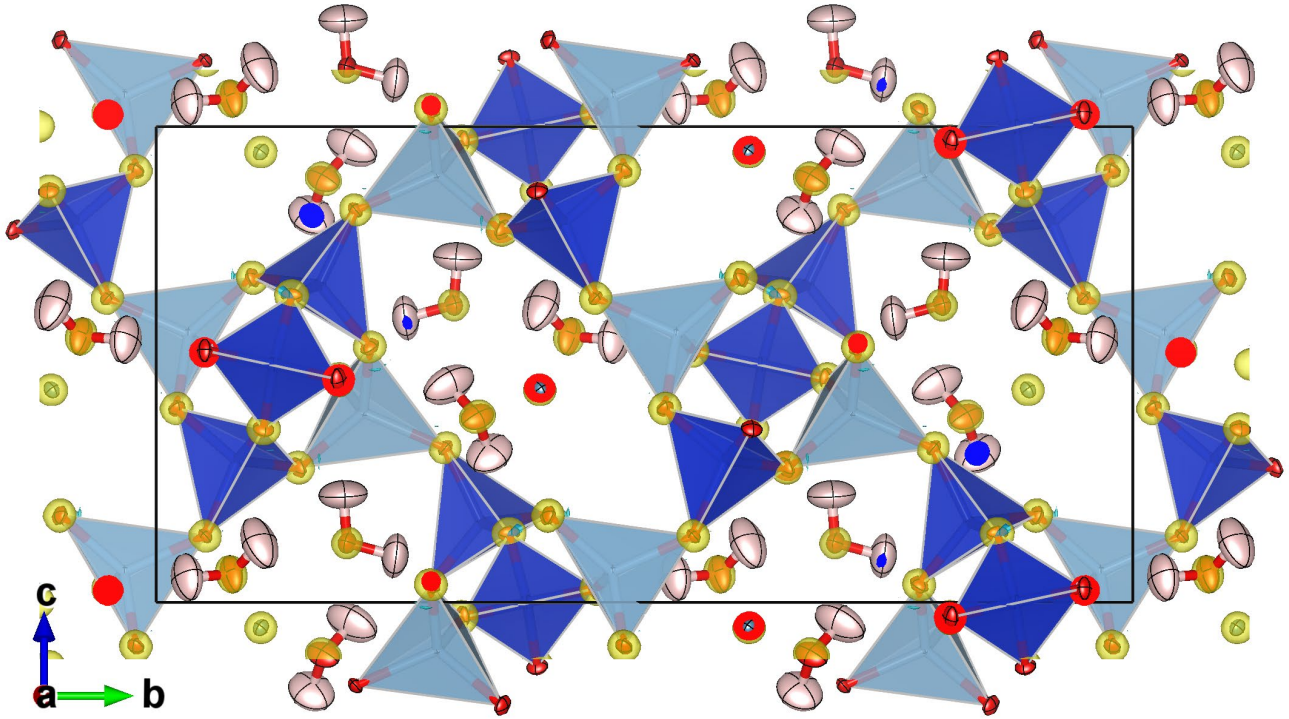
```
Single crystal Rw(Fo) =  0.038 for 22823 observations

          All data    I>0.0    I>3*sigI

NREFL=       22823     22823       22303
Rw(F**2)     0.076     0.076       0.076
R(F**2)      0.074     0.074       0.074
Rw(F)        -----     0.038       0.038
R(F)         -----     0.043       0.042
```



Neutron Structure from GSAS Refinement



Overlay of Fobs to the Neutron Structure



SHELX2016

```
TITL Scolecite from Neutron TOF Laue
REM  Space group Cc
CELL   0.70000   6.5120  18.9545   9.7582  90.000 108.921  90.000
ZERR      4      0.0001   0.0004   0.0002   0.000   0.001   0.000
LATT   -7
SYMM   +X,-Y,1/2+Z
SFAC  Al       0.00000  0.00000  0.00000  0.00000  0.00000  0.00000 =
         0.00000   0.00000   3.44900   0.000   0.000     0.072   1.430  26.982
SFAC  Ca       0.00000  0.00000  0.00000  0.00000  0.00000  0.00000 =
         0.00000   0.00000   4.70000   0.000   0.000     0.170   1.970  40.078
SFAC  H        0.00000  0.00000  0.00000  0.00000  0.00000  0.00000 =
         0.00000   0.00000  -3.73900   0.000   0.000    30.194   0.320   1.008
SFAC  O        0.00000  0.00000  0.00000  0.00000  0.00000  0.00000 =
         0.00000   0.00000   5.80300   0.000   0.000     0.001   0.660  15.999
SFAC  Si       0.00000  0.00000  0.00000  0.00000  0.00000  0.00000 =
         0.00000   0.00000   4.14910   0.000   0.000     0.052   1.170  28.086

UNIT  8   4   24   52  12
TEMP   -173
ACTA  50.0

SIZE  1.63 1.19 0.62
L.S. 5
BOND $H
eqiv $1 x,-y+1,Z+1/2
eqiv $2 x+1,y,z+1
eqiv $3 x-1/2, -y+1/2,z+1/2
eqiv $4 x,y,z+1
eqiv $5 x-1,y,z
HTAB O11 O10_$1
HTAB O11 O3_$2
HTAB O12 O4_$3
HTAB O12 O9_$4
HTAB O13 O6_$3
HTAB O13 O7_$5
HTAB O13 O5_$5
CONF
FMAP -2
PLAN -10
CONN 4 $Al $Si
LIST 3

WGHT    0.020900
FVAR       0.31665
CA1   2    0.108325    0.392807    0.446642    11.00000    0.00549    0.00402 =
         0.00445   -0.00039    0.00195    0.00026
```

Or add NEUT before SFAC in the .ins file for neutron structure refinement

NEUT
SFAC Al Ca H O Si

- Run ref2hk program from the GSAS folder

  $ ../../reduction/ref2hkl

  Select option 8 as the output format

- Copy SCOLECITE100K.hkl to a working folder

  $ cd /SNS/TOPAZ/IPTS-12132/shared/refine/SHELX

- Refine the scolecite structure

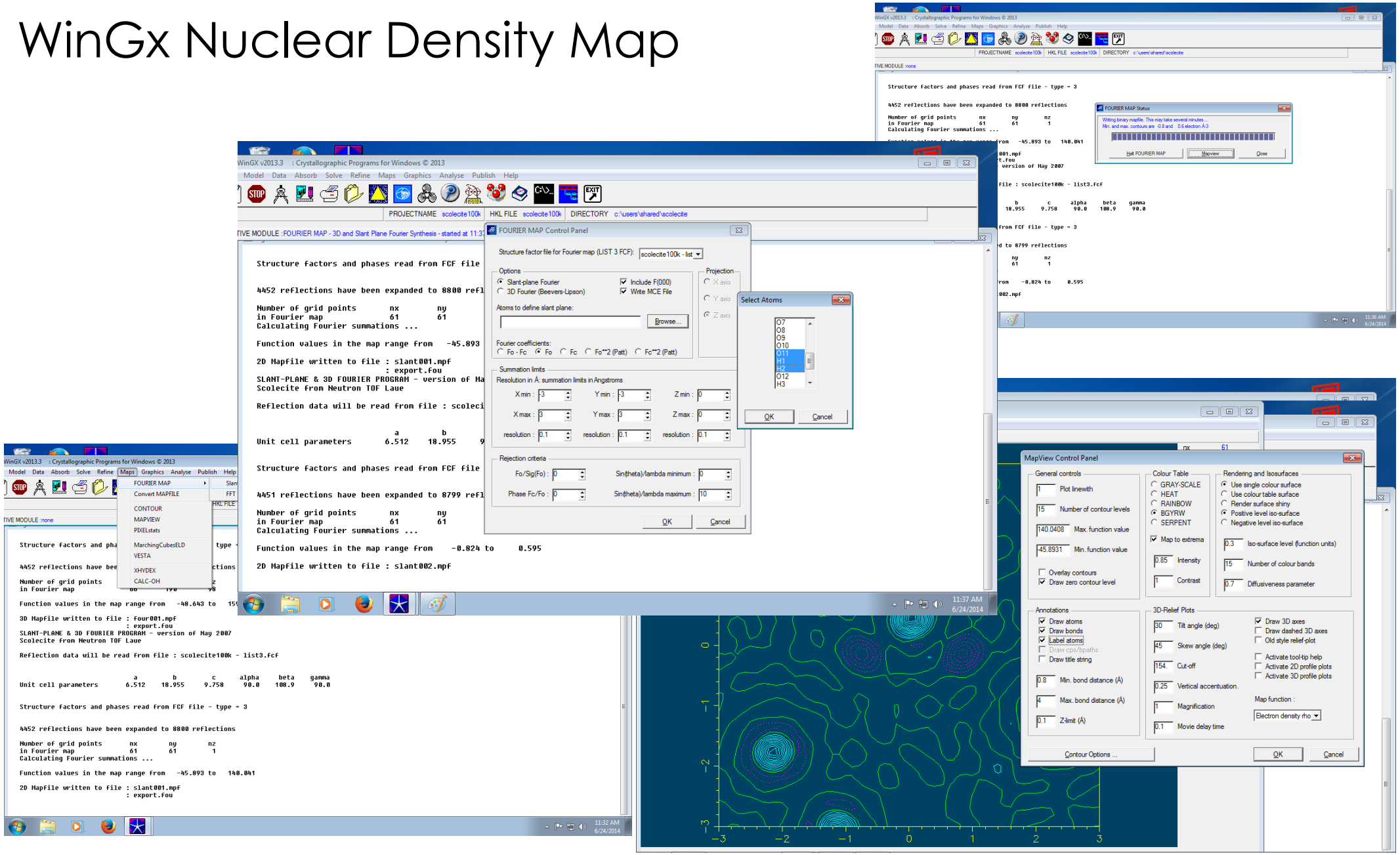
- $ ../shelx2013/shelxl scolecite100k

SHELX2016

wR2 = 0.0573 for 8171 data
and 2 / 226 parameters
GooF = S = 1.069;
Restrained GooF = 1.068 for 2 restraints
R1 = 0.0306
for 8151 Fo > 4sig(Fo) and 0.0307
for all 8171 data
wR2 = 0.0573,
GooF = S = 1.069,
Restrained GooF = 1.068 for all data

```
5xw@biganalysis04:/SNS/TOPAZ/IPTS-12132/shared/refine/SHELX
File  Edit  View  Search  Terminal  Help
[5xw@biganalysis04 GSAS]$ cd /SNS/TOPAZ/IPTS-12132/shared/refine/SHELX
[5xw@biganalysis04 SHELX]$ ls
scolecite100k.cif  SCOLECITE100K.hk4  scolecite100k.ins  scolecite100k.res  shelxl.lst     wingx.log
scolecite100k.fcf  scolecite100k.hkl  scolecite100k.lst  scolecite.lst      wgxScreen.log
[5xw@biganalysis04 SHELX]$ ../shelx2013/shelxl scolecite100k

 ++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
 +  SHELXL -  CRYSTAL STRUCTURE REFINEMENT  -   MULTI-CPU VERSION  +
 +  Copyright(C) George M. Sheldrick 1993-2014     Version 2014/3  +
 +  scolecite100k              started at 17:18:31 on 25-Jun-2014  +
 ++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++

 Command line parameters: scolecite100k -a50000 -b3000 -c624 -t19

 -a sets the approximate maximum number of atoms including hydrogens.
 -b sets the maximum number of full-matrix parameters (leave unchanged for
 CGLS). For example -b9000 allows refinement of 1000 anisotropic atoms or
 3000 with BLOC 1. For a 32-bit version, -b times the square root of the
 number of threads should not exceed about 65500. -c sets the reflection
 buffer size. This depends on the CPU cache size but will rarely need
 changing. -t sets the number of threads, otherwise the multi-CPU version
 sets this equal to the number of available CPUs. For optimal performance
 on systems with hyperthreading, usually the hyperthreading should be
 switched off or -t used to halve the number of threads; e.g. -t4 rather
 than -t8 for an Intel i7 processor.

 Running 19 threads on 32 processors

 Read instructions and data

 ** Warning: DISP instructions may be required for this wavelength **
 Data:    8171 unique,      0 suppressed   R(int) = 0.0598   R(sigma) = 0.0583
 Systematic absence violations:    0    Bad equivalents:    2
 wR2 = 0.0573 before cycle   1 for    8171 data and    226 /    226 parameters
 GooF = S =     1.069;     Restrained GooF =      1.068 for       2 restraints
 Mean shift/esd =   0.007  Maximum =     0.026 for  U23 O2          at 17:18:32
 Max. shift = 0.000 A for Al2      Max. dU = 0.000 for O4
 wR2 = 0.0573 before cycle   2 for    8171 data and    226 /    226 parameters
 GooF = S =     1.068;     Restrained GooF =      1.068 for       2 restraints
 Mean shift/esd =   0.002  Maximum =     0.010 for  U23 O2          at 17:18:32
 Max. shift = 0.000 A for Al2      Max. dU = 0.000 for O4
 wR2 = 0.0573 before cycle   3 for    8171 data and    226 /    226 parameters
 GooF = S =     1.068;     Restrained GooF =      1.068 for       2 restraints
 Mean shift/esd =   0.000  Maximum =    -0.001 for  OSF           at 17:18:32
 Max. shift = 0.000 A for H1      Max. dU = 0.000 for H3
 wR2 = 0.0573 before cycle   4 for    8171 data and    226 /    226 parameters
 GooF = S =     1.068;     Restrained GooF =      1.068 for       2 restraints
 Mean shift/esd =   0.000  Maximum =    -0.001 for   y  O8          at 17:18:32
 Max. shift = 0.000 A for O8      Max. dU = 0.000 for H4
 wR2 = 0.0573 before cycle   5 for    8171 data and    226 /    226 parameters
 GooF = S =     1.068;     Restrained GooF =      1.068 for       2 restraints
 Mean shift/esd =   0.000  Maximum =     0.001 for   y  O5          at 17:18:32
 Max. shift = 0.000 A for Al1      Max. dU = 0.000 for H4
 wR2 = 0.0573 before cycle   6 for    8171 data and      2 /    226 parameters
 GooF = S =     1.069;     Restrained GooF =      1.068 for       2 restraints
 R1 =  0.0306 for    8151 Fo > 4sig(Fo)  and  0.0307 for all    8171 data
 wR2 =  0.0573,  GooF = S =   1.069,  Restrained GooF =    1.068  for all data
     0  atoms may be split and     0  atoms NPD
 R1 =  0.0256 for   4407 unique reflections after merging for Fourier
 Highest peak    1.09  at  0.5811  0.0596  0.1236  [  0.65 A from O2 ]
 Deepest hole   -0.76  at  0.7053  0.4237  0.0474  [  0.63 A from O10 ]

 ++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
 +  scolecite100k finished at 17:18:33   Total elapsed time:      1.88 secs  +
 ++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
[5xw@biganalysis04 SHELX]$
```

WinGx Nuclear Density Map



TOPAZ Data Format SHELX HKLF2 Laue + TOF

```
hklFile.write( 3*'%4d' % (h, k, l)
    + 2*'%8.2f' % (fsq, sigfsq)
    + '%4d' % hstnum
    + 2*'%8.5f' % (wl, tbar)
    + 6*'%9.5f' % (dir_cos_1[0], dir_cos_2[0], dir_cos_1[1], dir_cos_2[1], dir_cos_1[2], dir_cos_2[2])
    + '%6d' % (curhst)
    + '%7d' % (seqnum)
    + '%7.4f%4d%9.5f%8.4f%7.2f%7.2f\n'
    +  % (transmission, dn, twoth, dsp, col, row) )
```

h, k, l	peak indices
fsq	peak intensity
sigfsq	sigma
hstnum:	a number from 1 to the number of crystal settings
wl:	neutron wavelength
tbar:	the absorption weighted path length
dir_cos_1:	the three direction cosines of a*, b* and c* with the reverse incident beam
dir_cos_2:	the three direction cosines of a*, b* and c* with the scattered beam
curhst:	the actual run number
seqnum:	a number from 1 to the number of peaks
transmission:	the transmission after absorption
dn:	the detector number
twoth:	2-theta angle
dsp:	d-spacing
col:	detector column pixel number
row:	detector row number