

WildFire

User Manual

The calculation of three-dimensional powder X-ray diffraction patterns for mica polytypes, illite/smectite and chlorite, and their fitting to measured patterns

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1. Introduction

WildFire calculates three-dimensional X-ray diffraction patterns for randomly oriented powders of mica (illite), illite/smectite (I/S) and chlorite. Intensities are computed by a three-dimensional integration in the reciprocal-space construct of Brindley and Méring (1951).

Newmod III models the basal 00*l* reflections of oriented mounts, which depend only on how the layers follow one another along the stacking direction. WildFire models what that leaves out, the way each layer sits in its own plane relative to the next:

- **Rotational stacking disorder.** Rotations between neighbouring layers, from the ordered *1M* structure to the fully disordered *1Md*, broaden and merge the hk*l* reflections into bands. In I/S, the expandable interlayers also break the coherence of the hk*l* reflections (section 4).
- **Polytypes.** Mica polytypes (*1M*, *1Md*, $2M_1$, *3T*) and chlorite polytypes (sections 5 to 7). Separating detrital, high-temperature $2M_1$ mica from diagenetic *1M* and *1Md* illite matters for burial diagenesis, thermal history and illite K–Ar and Ar–Ar dating.

Newmod III and WildFire. The two programs answer different questions and need different samples:

	Newmod III	WildFire
Sample mount	Oriented aggregate	Randomly oriented powder
Reflections	Basal 00*l*, along the stacking direction	Three-dimensional hk*l*
What it determines	Layer proportions (% smectite), Reichweite, chemistry (Fe, K), crystallite size	Mica and illite polytypes (*1M*, *1Md*, $2M_1$), chlorite polytypes, rotational disorder
Main use	Swelling behavior, mixed-layer ratios and the amount of each phase	Detrital versus diagenetic origin, and how disordered the stacking is

The program was first written by R. C. Reynolds, Jr. in 1993 and later moved to Java. This version keeps the original calculations and adds new tools around them:

- **Four solutions** chosen from the Solutions menu: Disordered micas (1M to 1Md and 3T to 3Td), Ordered polytypes, Chlorite, and the Peak Intensities Calculator.
- **Live plotting.** The diffractogram recalculates as you move a slider. There is no separate Run step.
- **Observed data.** Load a measured pattern, overlay it on the simulation, show the difference curve, auto-scale and remove background.
- **Fit Model.** Pick the parameters to free on Fit Settings and let the optimizer fit the simulation to the observed pattern.
- **Multiphase patterns.** Add up to four phases, from any of the solutions, and let the program fit their proportions, or their proportions and each phase's model together.

- **Reference minerals.** Add quartz, feldspars, carbonates and other non-clay minerals from a built-in library, or your own measured patterns, and fit them with the clay phases and a smooth background.
- **Fit Report.** After every fit, a report says how well the measured pattern determines each fitted value and which values trade off against each other.

This manual keeps the science from the 1993 manual and rewrites the operating instructions for the current program. Section 4 explains the science, sections 5 to 8 each solution, and sections 9 to 12 the tools and files shared by all of them.

2. Installing and starting

WildFire installs from a single Windows installer, `WildFire-1.0.1.msi`, and needs nothing else: the Java runtime it uses is included.

1. Double-click `WildFire-1.0.1.msi`.
2. If Windows shows "Windows protected your PC", click **More info**, then **Run anyway**. The installer is not digitally signed, which causes this notice.
3. Accept the license agreement, choose the installation folder (the default is `C:\Program Files\WildFire`) and click through to **Finish**.
4. Start the program from the desktop shortcut or the Start menu, or press the Windows key, type `WildFire` and press Enter.

The WildFire data folder. The first time it runs, WildFire creates a folder named `WildFire` in your user folder (for example `C:\Users\<your name>\WildFire`) and fills it with its starting files. Files you edit there are kept; a file you delete is recreated at the next start.

Folder	Contents	Used by
`acfiles`	Mica atomic coordinates in orthogonal space: `dritsc.txt`, `dritst.txt`, `dritsm.txt`, `veblen.txt`	Disordered and Ordered
`inputfile`	`inputfile.txt`, a crystallite thickness distribution	Disordered
`chlorite_acfiles`	Chlorite polytype coordinates: `chl.iaa.txt`, `chl.iab.txt`, `chl.iba.txt`, `chl.ibb.txt`, `chl.iib.txt`	Chlorite
`chlorite_inputfile`	`chlorite_inputfile.txt`, a chlorite thickness distribution	Chlorite
`intensities_acfiles`	Monoclinic-space coordinates for micas and chlorites	Peak Calculator
`experimentalFiles`, `modelFiles`	Empty folders offered as a place to keep your measured and saved patterns	You
`Minerals`	Your own reference-mineral patterns; created the first time you click **Minerals Folder...**	Multiphase (section 11)

New coordinate files placed in `acfiles` or `chlorite_acfiles` appear in the program's lists the next time WildFire starts (section 12).

What is installed

Item	Location
Program and Java runtime	The installation folder
License for WildFire	`LICENSE.txt` in the installation folder's `app` folder
Licenses for JFreeChart, Apache Commons Math, FlatLaf, the Noto Sans font and Java	The `app\licenses` folder, and **Help > About WildFire... > Licenses...**
This manual	The `app\docs` folder, when supplied with the installer

Uninstalling. Open Windows **Settings > Apps > Installed apps**, find WildFire and choose **Uninstall**. Your `WildFire` data folder is left in place; delete it yourself if you no longer need it.

Upgrading. Run the newer installer; it replaces the older version.

Decimal separator. Measured data files must use a period as the decimal point, whatever the Windows regional settings.

3. The main window

Everything happens in one window: the model's inputs on the left, the plot at the upper right, and below the plot two tabs, **Diffractogram** and **Multiphase**, that hold the tools. The tab you choose sets the view, and the plot above follows it: **Diffractogram** is the single-phase view, for one model, and shows its pattern; **Multiphase** is the multiphase view, for a mixture of phases, and shows their weighted sum. Each tab holds its own fit buttons and its own Plot Settings, Fit Settings and other tabs. The pattern is recalculated each time you move a slider or change a selection; there is no Run step.

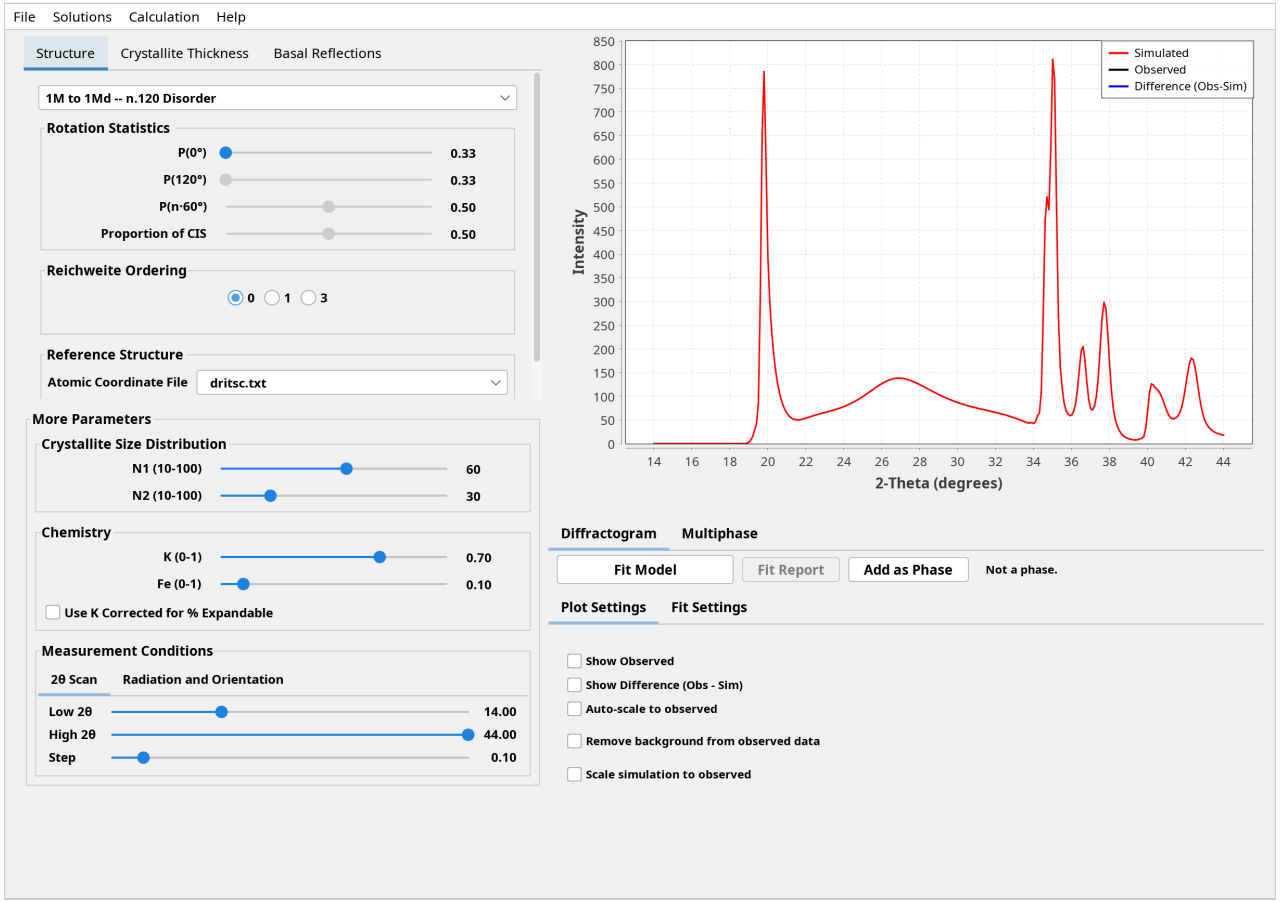


Figure 1. The WildFire main window with the Disordered solution.

Menus

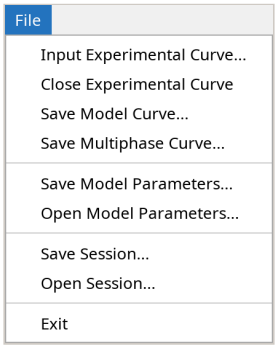


Figure 2. The File menu.

Menu	Item	What it does	Section
File	Input Experimental Curve...	Reads a measured pattern (two columns: 2θ and intensity)	9
File	Close Experimental Curve	Unloads the measured pattern; the plot settings that need it are cleared	9
File	Save Model Curve...	Writes the simulated pattern to a text file	12
File	Save Multiphase Curve...	Writes the multiphase pattern (the weighted sum of the phases) to a text file	11
File	Save Model Parameters...	Saves the model of the solution on screen, and the measured pattern, in one `.wfm` file	12
File	Open Model Parameters...	Reopens a `.wfm` model into its solution	12
File	Save Session...	Saves everything: all three solutions, the measured pattern and the phases, in one `.wfs` file	12
File	Open Session...	Reopens a saved session	12
File	Exit	Closes WildFire	
Solutions	Disordered	Rotationally disordered micas and illite/smectite (1M to 1Md, 3T to 3Td, cis/trans interstratification)	5
Solutions	Chlorite	Chlorite polytypes, single or interstratified	7
Solutions	Ordered	Ordered mica polytypes and thick crystallites	6
Solutions	Peak Calculator	Position and intensity of a single hkl reflection	8
Calculation	Stacking Method	How the stacking statistics are summed: Reynolds or Kakinoki–Komura (below)	3
Help	About WildFire...	Version, credits and licenses	

The window title names the solution in use, for example "WILDFIRE - Disordered". The program starts in the Disordered solution. Each solution keeps its own settings, so you can switch back and forth without losing them; the measured pattern stays loaded across all of them.

Left side: the model. The upper panel holds the tabs that describe the structure. They differ by solution (Structure, Crystallite Thickness and, for Disordered, Basal Reflections). The More Parameters panel below holds the crystallite size (N1 and N2), the chemistry, and Measurement Conditions, which has a 2θ Scan tab and a Radiation and Orientation tab (section 9). A panel taller than its space has a scroll bar.

Upper right: the plot. In the single-phase view the plot shows the simulated pattern in red, and, when switched on, the measured pattern in black and the difference curve in blue. In the multiphase view it shows the weighted sum of the phases and reference minerals you have added (section 11) in the same colours.

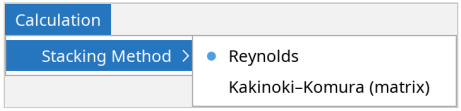
- Move the pointer over a plot to read its 2θ and the matching d-spacing, calculated from Bragg's law with the selected wavelength, in a small box under the legend.
- Drag a rectangle from upper left to lower right to zoom in; drag in the opposite direction to return to the full view.
- Right-click the plot for the standard chart menu: copy, save as an image, print, zoom and chart properties.

Lower right: the view tabs.

Tab	Buttons	Tabs inside
Diffractogram (single-phase view)	**Fit Model** fits the current solution to the measured pattern; **Fit Report** shows how well the last Fit Model determined each parameter (both section 10); **Add as Phase** stores the model as a phase (section 11). A line beside them says whether the model in the panel is one of the phases.	**Plot Settings** (section 9), **Fit Settings** (section 10)
Multiphase (multiphase view)	**Fit Weights** and **Fit Models** fit the phases, reference minerals and background; **Fit Report** shows the report on the last of these fits (section 11).	**Plot Settings**, **Fit Settings** (each phase's ticks), **Phases** and **Minerals** (section 11)

The Plot Settings boxes are shared: a box ticked in one view is ticked in the other. The plot keeps the same width and size in both views, so the two can be compared by switching tabs.

Calculation menu



The Calculation menu, with Stacking Method open.

Calculation > Stacking Method chooses how WildFire adds up its stacking statistics: the sums, over every pair of layers in a crystallite, of the phase factors produced by the rotations and shifts between them. The choice applies to all three solutions (Disordered,

Ordered and Chlorite), to the basal 00l reflections of illite/smectite, with or without Run in Parallel, and to every pattern calculated by Fit Model, Fit Weights and Fit Models. The Peak Intensities Calculator does not use stacking statistics and is not affected.

Choice	How the sum is calculated
Reynolds	The original WildFire calculation (Reynolds, 1993), which follows every accumulated layer shift and counts how often each one occurs; the basal reflections use the domain frequencies of Bethke and Reynolds (1986). The default.
Kakinoki–Komura (matrix)	The same sums as a product of transition matrices (Kakinoki and Komura, 1952, 1965; Drits and Tchoubar, 1990). The same pattern, calculated faster, much faster for the Two-Mica (Cis-Trans) models.

How Kakinoki–Komura works. The stacking is written as a matrix P of transition probabilities between layer states: a layer rotation, a cis- or trans-vacant layer, a chlorite layer type, or, for the basal reflections, a layer type and its neighbours (Drits and Sakharov, 1976). Each transition is multiplied by the phase factor of the lateral shift (or basal spacing) it adds, so the sum over every stacking sequence of n layers becomes the n-th power of one small matrix, and the accumulated shifts never have to be listed.

What the choice does not change. Both use Reynolds' model throughout: layer structures and scattering factors, rotation and ordering probabilities, crystallite sizes, the reciprocal-space integration, and the Lorentz-polarization and orientation corrections. Only the summation differs, and because both methods are exact they agree to rounding error: compared on several thousand random models in all three solutions, the statistics agreed to about 10^{-13} and the patterns were identical. Choosing Kakinoki–Komura therefore does not make WildFire equivalent to programs built on the complete approach of Drits and co-workers, which make different physical choices and can give different patterns for the same nominal inputs; the agreement shows the sum is calculated correctly, not that the two models agree.

The choice is remembered the next time WildFire starts. It cannot be changed while a fit is running: each fit uses the method that was selected when it started.

4. Background: how WildFire models a pattern

WildFire calculates the diffraction pattern of a random powder by integrating the scattered intensity over reciprocal space, following Brindley and Méring (1951). This section, carried over from the 1993 manual, explains the structures and parameters the calculation uses.

Layer types and atomic coordinates

The mica coordinate files supplied with WildFire are those of Drits et al. (1984) for their *C*, *M* and *T* layers, plus one from Guthrie and Veblen (1989).

File	Layer	Description
`dritst.txt`	*T*, *trans*-vacant (*tv*)	The common mica structure: the vacant octahedral site lies on the mirror plane, space group *C*2/*m*
`dritsc.txt`	*C*, *cis*-vacant (*cv*)	*M*1 site occupied and one of the *cis* (*M*2) sites vacant; non-centrosymmetric, space group *C*2 (Reynolds, 1993; Drits et al., 1993)
`dritsm.txt`	*M*	An average of the two: all three octahedral sites 2/3 filled (*C*2/*m*)
`veblen.txt`	Guthrie and Veblen (1989)	More tetrahedral tilt than the *T* layer of Drits et al. (1984)

Each file has been transformed to orthogonal space, and must be, to work in WildFire. The first line holds, in order, a label, *a*, *b*, *c*, β and the number of atom lines that follow. Each later line holds an atom label, the site occupancy and the orthogonal fractional coordinates *x*, *y* and *z*. A typical file:

```
DRITS.T, 5.199, 9.005, 10.164, 101.3, 11
K, 1, -.1915, 0, .5
OX, 2, -.4565, -.272, .335
OX, 2, -.4565, .272, .335
OX, 2, -.1415, .5, .32
SI, 2, -.1865, .329, .27
SI, 2, -.1865, -.329, .27
OX, 2, -.1935, -.309, .108
OX, 2, -.1935, .309, .108
OH, 2, -.1215, 0, .108
AL, 1, .5, .333, 0
AL, 1, .5, -.333, 0
```

Any set of coordinates written in this form can be added (section 12). The interstratified *cis*/*trans* options always use `dritsc.txt` and `dritst.txt`, whatever file is selected. Their statistical matrices are tuned to the monoclinic angles of those two cells, 99.1 ± 0.1° and 101.3 ± 0.1°. With coordinates for cells of other angles, the output will look real, and perhaps interesting, but may be nonsense.

Half and full cells. `dritst.txt`, `dritsm.txt` and `veblen.txt` list only the top half of the cell (*z* from 0 to 0.5), with the occupancy of each atom off the octahedral plane doubled to stand for its partner through the centre of symmetry at the origin. For such a cell the

structure factor is the cosine sum alone, and that is exact. `dritsc.txt` has no centre of symmetry, so it lists the whole cell, z from −0.5 to 0.5. The Ordered 1M and 1M-Interstratified calculations add the sine part of the structure factor only for a full cell, one that lists atoms below the octahedral plane ($z < -0.1$); for `dritsc.txt` in 1M, only with Single Enantiomorph ticked. Disordered and the other ordered polytypes always use the cosine sum, which for the *cis*-vacant cell means equal proportions of its two hands.

Structure factors are calculated from atomic scattering factors computed by the method of Wright (1973), corrected for isotropic thermal vibration by multiplying by $\exp(-2B \sin^2\theta / \lambda^2)$, with B = 1.5 for cations and B = 2 for anions. Throughout this manual λ = 1.5418 Å (Cu Kα).

Rotational disorder and the parameter P_0

Stacking disorder in micas is described by rotations of each 2:1 layer relative to the layer beneath it, by 60, 120, 180, 240 or 300°.

- **P_0**, the probability of a zero rotation, sets the order. $P_0 = 0.6$ describes crystallites in which, on average, 60% of the layers are not rotated relative to the layer beneath, 20% are rotated 120° and 20% are rotated 240°, at random. $P_0 = 1$ is the ideal *1M* structure, and $P_0 = 1/3$ (equal numbers of 0, 120 and 240° rotations) is the fully disordered limit, *1Md*.
- **n·120° disorder** uses rotations of 0, 120 and 240° only. **n·60° disorder** adds rotations of 60, 180 and 300°; their share of all non-zero rotations is P_{60}. With $P_{60} = 0$ the result is the same as n·120° disorder; with $P_{60} = 1$ every non-zero rotation is 60, 180 or 300°; with $P_{60} = 0.6$, the non-zero rotations are spread equally and at random over 60, 120, 180, 240 and 300°.
- **3T to 3Td** uses P_{120}, the probability of a 120° rotation. $P_{120} = 1$ gives a screw axis along Z in which each layer is rotated 120° from the one below: the *3T* polytype. $P_{120} = 1/3$ gives *1Md*, the same as $P_0 = 1/3$. Between these limits the screw axis is progressively disordered by zero rotations and out-of-sequence 240° rotations. WildFire sums the patterns of the two enantiomorphs, with right- and left-handed screw axes: for $P_{120} = 0.7$, one has $P_0 = P_{240} = 0.15$ and the other has $P_{240} = 0.7$ and $P_0 = 0.15$.
- **P_cv**, the proportion of *cis*-vacant cells, sets the abundance of *cv* layers randomly interstratified with *tv* layers.

Two definitions of P_0. WildFire defines a rotation relative to the layer beneath ("interlayer" rotations; Reynolds, 1993). Drits and his co-workers define it relative to the absolute azimuthal direction, $-X$ (Drits et al., 1984; Drits and Tchoubar, 1990). The two agree at $P_0 = 1$ and $P_0 = 1/3$, but in between the azimuthal P_0 is always the larger.

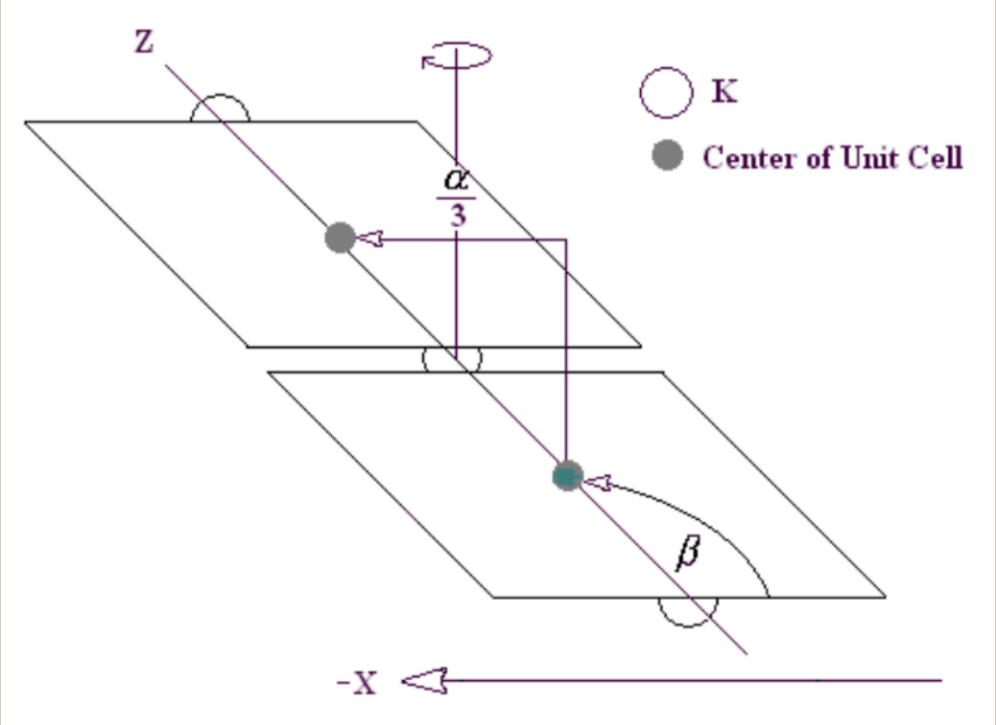


Figure 3. Two mica 2:1 layers stacked in the 1M pattern.

In the ideal *1M* stacking, the center of each unit cell is displaced from the one beneath it by $-a/3$. A stacking sequence can be drawn as a chain of stacking vectors of length $a/6$ viewed down the rotation axis.

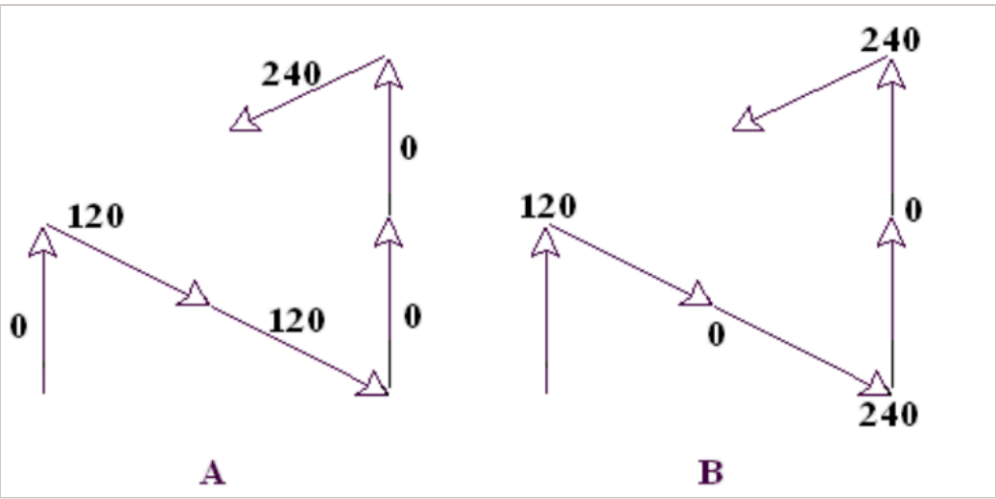


Figure 4. The same stacking sequence drawn with azimuthal (A) and interlayer (B) rotations.

Arrays A and B give identical diffraction patterns, and $P_0 + P_{120} + P_{240} = 1$ in both, but their probabilities differ. Array A, indexed to the azimuthal direction, occurs with probability $P_0 \cdot P_{120} \cdot P_{120} \cdot P_0 \cdot P_0 \cdot P_{240}$. Array B, indexed to the layer beneath, has one term fewer, because there is one fewer interlayer than layers: $P_{120} \cdot P_0 \cdot P_{240} \cdot P_0 \cdot P_{240}$.

An empirical comparison of patterns calculated both ways over $P_0 = 1/3$ to 1 gives a logarithmic relation forced through (1, 1):

$$P_0(\text{azimuthal}) = 1.0017 + 1.3830 \log_{10} P_0(\text{interlayer})$$

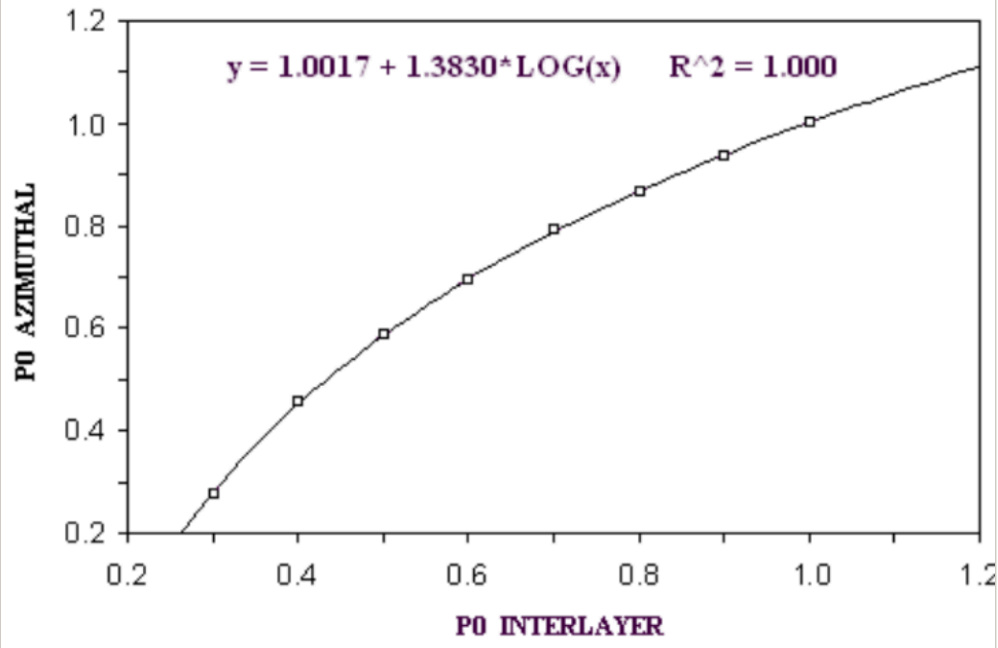


Figure 5. Comparison between the two definitions of P_0 that give equivalent diffraction patterns.

For example, P_0 (interlayer) = 0.7 matches P_0 (azimuthal) = 0.787. The matching patterns are not exactly the same: the azimuthal option slightly enhances the $\bar{1}13$ reflection, noticeably only for the *tv* structure.

Crystallite size

N1 and N2 are the numbers of unit cells along *X* and *Y*. The defaults, 60 and 30, work well for most illite and I/S; a hairy illite may need attention. Values below 10 cannot be used: WildFire assumes the structure factors and phase shifts are constant across each *hk* rod, and below 10 the rod cross-sections become large enough to break that assumption.

N3, the number of unit cells along *Z*, is given as a distribution of crystallite thicknesses. It can be read from an INPUTFILE, calculated from a mean defect-free distance and a maximum N3, or, for I/S, counted from the Reichweite and expandability (below).

The ripple near 19.2° 2θ in *tv 1M* patterns is a Fourier-series artifact of a fixed crystallite shape in *X* and *Y*. It is the only such artifact the author found in hundreds of calculated patterns; a distribution of *X* and *Y* sizes would remove it, but at too great a cost in computing time.

Basal reflections and I/S

The basal (00*l*) series is calculated separately from the three-dimensional (*hkl*) pattern, and the two are added after suitable weighting. They must be treated separately for I/S because the coherence along *Z* differs. The 00*l* coherence extends over illite stacks and expandable interlayers to the limit of the MacEwan crystallite. The expandable

interlayers are turbostratic defects, so *hkl* diffraction comes only from thin stacks of illite: the fundamental particles of Nadeau et al. (1984). A random powder of I/S therefore diffracts like a powder of very thin illite crystallites (Reynolds, 1992). In the language of Nadeau and co-workers, interparticle diffraction occurs in one dimension (00*l*) but not in three (*hkl*).

Counting illite particles in I/S crystallites

When the crystallite thickness is calculated from the Reichweite (R) and the decimal fraction expandable (P_ex), WildFire generates every combination of illite and expandable interfaces in MacEwan crystallites of N = 1, 2, 3 ... layers. The procedure resembles that of Altaner and Bethke (1988), except that a range of MacEwan crystallite thicknesses is used, weighted by the Ergun (1970) defect-broadening model. This gave better agreement with measured patterns.

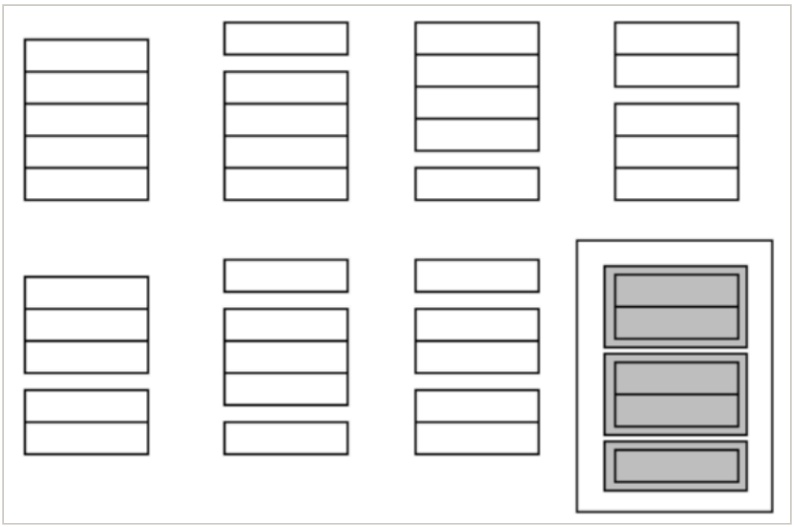


Figure 6. All MacEwan crystallites for N3 = 5 and R = 1. The boxed one contains two 20-Å particles and one 10-Å particle.

For example, let P_S be an expandable interlayer and P_I an interlayer collapsed about a K ion. For R = 1 and P_ex = 0.2, P_S.I = 1, P_I.S = 0.25, P_I.I = 0.75 and P_S.S = 0 (Reynolds, 1980). The boxed array occurs with frequency

$$\sigma_0 = P_S \cdot P_{S.I} \cdot P_{I.S} \cdot P_{S.I} = 0.2 \cdot 1 \cdot 0.25 \cdot 1 = 0.05$$

Weighting for the MacEwan crystallite thickness by defect-broadening theory, with δ the mean defect-free distance in layers,

$$\sigma = \sigma_0 \exp\left(-\frac{N-1}{\delta}\right)$$

With δ = 6, a value that works well for illite basal reflections, σ = 0.05 × 0.513 = 0.02565. This array contributes 2 × 0.02565 = 0.0513 20-Å particles and 0.02565 10-Å particles. Treating the other seven arrays the same way gives the numbers of 10-, 20-, 30-, 40- and 50-Å particles for 5-layer crystallites, and summing over N = 1, 2, 3 ... N3 gives the final distribution.

Crystallite end effects produce single layers (N = 1) for R > 0, and single, double and triple layers for R = 3. These are probably unrealistic, a weakness of the Markov approach, though Nadeau et al. (1984) show some R = 1 histograms with single 2:1 layers. Their abundances are reduced: single layers are multiplied by exp(−1) for R = 1, and 10-, 20- and 30-Å particles by exp(−3), exp(−2) and exp(−1) for R = 3. The distribution is then normalized to a sum of one.

Parts of the calculation are arbitrary, such as δ = 6 and the end-effect reductions. They are defended on the grounds that they reproduce measured patterns of a range of I/S structures very well (Reynolds, 1993), so well that any better approach would have to show itself within the intrinsic resolution of powder diffraction.

Potassium and preferred orientation

K corrected for expandability. This option calculates the mean K per Si_4O_{10} assuming 0.89 K per illite interlayer and 0.2 K on the surfaces of illite stacks or particles. K then falls as expandability rises in I/S (Środoń et al., 1992), or as crystallite thickness falls in pure illite. The 0.2 K on particle surfaces stands for the electrons in 0.4 Na or 0.2 Ca, matching the exchange capacity of a smectite-like surface.

Dollase factor. This corrects for preferred orientation by the method of Dollase (1986), based on the March function. A value of 1 means a random powder. Values below 1 strengthen reflections from planes whose normals lie near the normal to (001), and weaken those whose normals lie near the normal to (010). Refine it until the calculated 002/(110; 020) intensity ratio of illite matches the measured one. With good laboratory practice it rarely needs to go below 0.9, and many patterns need none. The correction does not work well for large departures from random orientation: if you need 0.8, improve the sample preparation instead. The orientation may not be unimodal either; with side, back or front loading, strong orientation may exist only at the sample surface.

5. Disordered micas and illite/smectite

The Disordered solution (**Solutions > Disordered**) models rotationally disordered micas, illite and illite/smectite, including random interstratification of *cis*- and *trans*-vacant cells. Its upper panel has three tabs: **Structure**, **Crystallite Thickness** and **Basal Reflections**. Controls that do not apply to the current choices are greyed out, so only relevant inputs are offered.

Structure tab

Choose one of five structures from the list at the top (shown open in section 3). Each enables a different set of **Rotation Statistics** sliders.

Structure	Enabled inputs	Coordinate file
1M to 1Md -- n.120 Disorder	P(0°)	Selected
1M to 1Md -- n.60 Disorder	P(0°), P(n·60°)	Selected
3T to 3Td -- n.120 Disorder	P(120°)	Selected
Two-Mica (Cis-Trans) 1M to 1Md -- n.120 Disorder	P(0°), Proportion of CIS	`dritsc.txt` and `dritst.txt`
Two-Mica (Cis-Trans) 1M to 1Md -- n.60/n.120 Disorder	P(0°), P(n·60°), Proportion of CIS	`dritsc.txt` and `dritst.txt`

Control	Range	Meaning (section 4)
P(0°)	0.33 to 1.00	Probability of a zero rotation, P_0
P(120°)	0.33 to 1.00	Probability of a 120° rotation, P_{120}
P(n·60°)	0 to 1.00	Fraction of non-zero rotations that are 60, 180 or 300°, P_{60}
Proportion of CIS	0 to 1.00	Fraction of *cis*-vacant cells, P_cv
Reichweite Ordering	0, 1 or 3	Ordering of illite and expandable interlayers in I/S (Reynolds, 1980)
Atomic Coordinate File	Files in `acfiles`	The layer structure, for the first three structures only

The structures are listed roughly in order of computing time, except the third. The interstratified options, the fifth above all, need exhaustive statistical calculations: for a 12-component system and N3 = 10, generating every stacking array directly would take 12^{10} arrays. WildFire uses matrices instead, which only works for the monoclinic angles of `dritsc.txt` and `dritst.txt`. Reichweite is used only when the Crystallite Thickness or Basal Reflections choice calls for I/S; otherwise it is greyed out.

Crystallite Thickness tab

This tab sets the distribution of crystallite thicknesses (N3) for the *hkl* reflections.

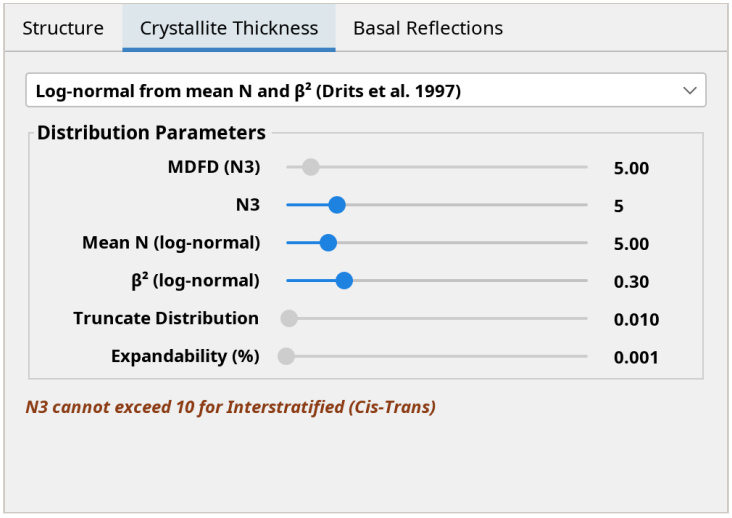


Figure 7. Crystallite Thickness tab with the log-normal option selected.

Option	Use it for	Inputs
Count illite particles in crystallites using Reichweite and % expandable	I/S	Reichweite (Structure tab), Expandability, Truncate Distribution
Read from INPUTFILE	Any thickness distribution you write yourself	`inputfile.txt` (section 12)
Calculated from defect-free distance and maximum N3	Pure illite or mica	MDFD (N3), the mean defect-free distance, 1 to 50; N3, the maximum, 1 to 25
Log-normal from mean N and β^2 (Drits et al. 1997)	Illite or mica whose thicknesses peak above one layer	Mean N, 1.0 to 30.0; β^2, 0.01 to 1.50; N3, the maximum, 1 to 25

The log-normal distribution. Drits, Środoń and Eberl (1997) found that the thicknesses of illite and I/S crystallites, measured by TEM and by the Bertaut–Warren–Averbach analysis of XRD peaks, follow a log-normal distribution closely. With this option the proportion of crystallites N layers thick is

$$f(N) \;\propto\; \frac{1}{N}\exp\left[-\frac{(\ln N-\alpha)^2}{2\beta^2}\right], \qquad \alpha=\ln\bar{N}-\frac{\beta^2}{2}, \qquad N=1,\ldots,N3$$

where $\bar{N}$ is **Mean N** (1.0 to 30.0 layers) and β^2 (0.01 to 1.50), the variance of ln N, sets the width. Unlike the defect-free (exponential) distribution, whose most common crystallite is always one layer thick, the log-normal one peaks at $\bar{N}e^{-3\beta^2/2}$ (4.4 layers for Mean N = 8 and β^2 = 0.40). N3 cuts the distribution off, so the mean actually used is a little below Mean N unless N3 is well above it: for Mean N = 8 and β^2 = 0.40 it is 7.3 with N3 = 20 and 7.8 with N3 = 30. In this solution N3 is at most 25 (10 for the Two-Mica structures), so a log-normal distribution with a large Mean N is truncated noticeably.

- **Expandability (%)** is the decimal fraction of expandable layers, P_ex, from 0.001 to 1.000 (despite the % in its label).
- **Truncate Distribution** (0.001 to 0.999) drops the thickest, rarest crystallites from the counted distribution. Going further adds little to the pattern but roughly doubles the run time for each extra N. Truncation at 0.01 has no visible effect, 0.05 barely detectable effects, and a large time saving; experiment to find what is acceptable. For example, 0.015 limits the series to N3 = 7 for R = 1 and P_ex = 0.2.
- For the two **Two-Mica (Cis-Trans)** structures with the defect-free or log-normal option, N3 cannot exceed 10. The panel says so in red and lowers N3 to 10 if needed.
- The **Crystallite Thickness Distribution** histogram, shown only with the first option, plots the relative abundance of each counted crystallite thickness. It is the theoretical counterpart of the particle-thickness histograms measured by Nadeau et al. (1984).

Remember that the shapes of *hkl* peaks are much less sensitive to crystallite thickness than the 00*l* peaks, because thickness is only one component of the crystallite size.

Basal Reflections tab

This tab sets how the 00*l* reflections are treated.

Option	Use it for	Inputs
They can be eliminated from the calculated pattern	Seeing *hkl* detail hidden under basal peaks	None
They describe a pure mica...	Pure illite or mica, whose coherence along Z is the same for basal and *hkl* reflections	None
They describe a mixed-layered structure...	I/S, whose basal coherence along Z is greater than for the *hkl* structure; the basal series is calculated by a NEWMOD-like routine	Mean D(z), Maximum N, Smectite Type, plus Reichweite and Expandability

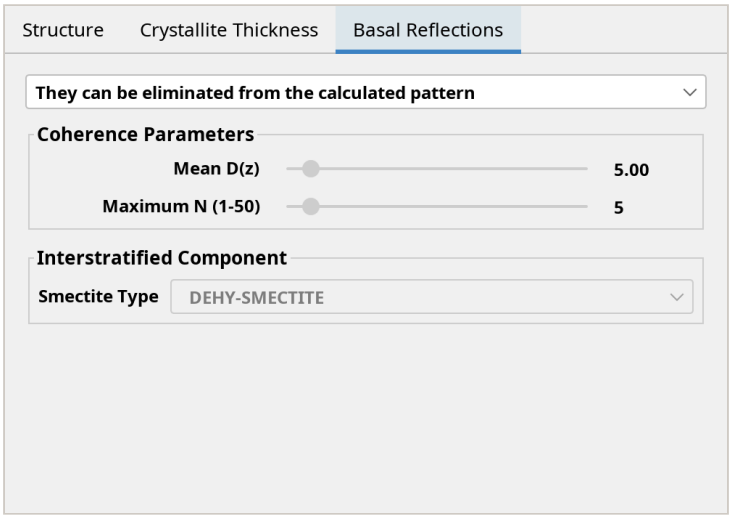


Figure 8. Basal Reflections tab, with Coherence Parameters and the Interstratified Component.

- **Mean D(z)** (1.00 to 50.00) is the mean defect-free (coherence) distance along *Z*, in layers, for MacEwan crystallites.
- **Maximum N (1-50)** is the largest crystallite in the basal calculation. Complete defect broadening needs Maximum N about seven times Mean D(z); three to five times is a good choice for illite.
- **Smectite Type** is the expandable component: DEHY-SMECTITE (dehydrated, d(001) = 9.65 Å), DISMECTITE-2GLY, DISMECTITE-1GLY, DISMECTITE-1WAT or DISMECTITE-2WAT.

Eliminating the basal reflections helps you study features such as the 022 reflection, which always lies under the illite 003 peak, and the effect of the 004 on the 02*l*; 13*l* signature between 34 and 39° 2θ.

More Parameters

Control	Range	Default	Meaning
N1 (10-100)	10 to 100	60	Unit cells along *X*
N2 (10-100)	10 to 100	30	Unit cells along *Y*
K (0-1)	0 to 1.00	0.70	K atoms per Si_4O_{10}
Fe (0-1)	0 to 1.00	0.10	Fe atoms per Si_4O_{10}; 0.1 puts 0.05 Fe in each octahedral site
Use K Corrected for % Expandable	On or off	Off	Calculates K from expandability or thickness instead of the K slider, which is then greyed out (section 4)

Measurement Conditions holds the 2θ scan and, on **Radiation and Orientation**, the Dollase factor and wavelength (section 9). For this solution the scan runs from 2.0 to at most 44.0° 2θ. The upper limit is set by the program's reciprocal-lattice geometry, and 16 to 44° holds all the information needed to interpret an illite or I/S pattern.

Worked examples

These three examples from the 1993 manual set up typical calculations. Start each from the defaults, set the scan to 16 to 44° with a step of 0.10, and leave N1 = 60, N2 = 30, Fe = 0.10 and Dollase = 1.00.

Example I: disordered *trans*-vacant illite.

1. Structure: **1M to 1Md -- n.120 Disorder**, coordinate file `dritst.txt`, P(0°) = 0.60.
2. Basal Reflections: **They describe a pure mica...**
3. Crystallite Thickness: **Calculated from defect-free distance and maximum N3**, MDFD (N3) = 5.0, N3 = 20.
4. Tick **Use K Corrected for % Expandable**.

The *1M tv* character shows in the strong $\bar{1}12$ and 112 reflections near 24 and 29° 2θ. Their large breadths, compared with the 20*l*; 13*l* (*k* = 3*n*) reflections between 34 and 39°, show stacking disorder of the semi-ordered n·120° type (Méring, 1975). The disorder is not turbostratic, or the 20*l*; 13*l* reflections would be smeared toward the twodimensional band shape of most smectites. It contains few or no n·60° rotations, because the region between 36 and 39° shows no tendency to form one intermediate peak instead of two (Reynolds, 1993). The 002 and 003 peaks look weak because real samples are rarely random; a Dollase factor of 0.95 or 0.9 may be needed to model many measured patterns.

Example II: thick illite crystallites with interstratified *cis*/*trans* cells and n·60° and n·120° disorder.

1. Structure: **Two-Mica (Cis-Trans) 1M to 1Md -- n.60/n.120 Disorder**, P(0°) = 0.80, P(n·60°) = 0.40, Proportion of CIS = 0.60. (For equal 60, 120, 180, 240 and 300° rotations, use P(n·60°) = 0.6.)
2. Basal Reflections: **They describe a mixed-layered structure...**, Smectite Type DEHY-SMECTITE, Mean D(z) = 6.0, Maximum N = 30.
3. Crystallite Thickness: **Read from INPUTFILE**, with `inputfile.txt` describing crystallites 10 layers thick (the supplied file does this).
4. Reichweite 0, Expandability 0.01, K = 0.70.

The structure is not I/S, so why the mixed-layer option? Realistic 00*l* peak shapes, without interpeak ripples, need a crystallite size distribution like that of the defectbroadening model. That distribution extends well beyond the mean thickness, to N3 values impractical for interstratified *cv*/*tv* cells: N3 = 20 would take hours. So model the 00*l* series accurately with the basal routine, and pick a single large N3 near the mean basal N for the *hkl* reflections. *hkl* peak shapes are less sensitive to N3, tend toward defect-broadened shapes when rotational disorder is present, and lose the ripples of a single thickness with even a little disorder. Dehydrated smectite at 1% expandable does not measurably change illite peaks, so this simulates a pure illite. For very thick crystallites without rotational disorder, use the Ordered solution instead (section 6), where N3 can reach 50.

Sharp 20*l*; 13*l* peaks show thick crystals. At P_0 = 0.8 few layers are rotated, so the n·60° rotations have little effect. The sharp 02*l*; 11*l* series shows little disorder, and the relatively strong 111 near 23° shows a significant *cv* component. The large apparent 003/002 ratio comes from the strong *cv* 022 peak lying almost exactly on the illite 003. With N3 = 9 instead of 10 the run would take about half as long, with little change: experiment with small N3 values first and work up.

Example III: illite/smectite with interstratified *cis*/*trans* cells and n·120° disorder. You will probably use this case more than any other, because most illites contain at least 5% expandable layers. Run times can be long at P_ex = 0.05 unless you truncate the distribution, but they fall quickly as expandability rises.

1. Structure: **Two-Mica (Cis-Trans) 1M to 1Md -- n.120 Disorder**, P(0°) = 0.70, Proportion of CIS = 0.30.

2. Basal Reflections: **They describe a mixed-layered structure…**, DEHY-SMECTITE, Mean D(z) = 6.0, Maximum N = 20.
3. Crystallite Thickness: **Count illite particles in crystallites using Reichweite and % expandable**, Truncate Distribution = 0.015.
4. Reichweite 1, Expandability 0.20, and tick **Use K Corrected for % Expandable**.

The pattern resembles Example I. The main difference is the broad signature between 36 and 39° 2θ: $k = 3n$ reflections, little affected by rotational disorder but broadened by the thin crystallites typical of I/S. The 0.3 proportion of *cv* layers produces no recognizable *1M cv* component, but it weakens the *tv 1M* Ī12 and 112 peaks near 24 and 29°.

Modeling a measured pattern

You should learn something from every pattern you calculate. With attention to the effect of each input, you will become able to interpret much of a measured pattern by inspection, and to "look through" interference from quartz, feldspar and similar minerals, though not other clay minerals.

Start with a good measured pattern. The orientation must be random or nearly so; freeze-drying is very good for this. The sample must be thick enough to give full intensity at the highest angles recorded, which takes 300 to 500 mg of powder. For I/S the dehydrated state is most convenient, because the useful *hkl* range then holds only one basal reflection, the illite 003. Rehydration can occur during the long runs, so the author enclosed the sample in a chamber with a thin plastic window, swept with tank nitrogen. A 2θ step of 0.05° counted for 20 to 40 s gives about 20,000 counts at the strongest peak, usually the 020; 110 near 19.8° 2θ. Slit choice matters little because the peaks are broad, but needlessly fine slits greatly increase counting time.

Study the 00*l* series first. Run an oriented aggregate air-dried and after ethylene glycol solvation, and analyze it with Newmod. For I/S, find P_ex and the Reichweite; they are needed for the mixed-layer basal option and the counted thickness option. The 00*l* study can also confirm the default Fe = 0.1: much more Fe shows as a weak illite 002, or I/S 002/003 if quartz is absent. Find parameters that give the right peak breadths with the smallest Maximum N. Defect broadening is WildFire's greatest consumer of computing time, and with the fifth structure option you probably cannot afford the parameters the defect-broadening model calls for. A perfect fit to 00*l* peak shapes is unnecessary: their nuances disappear in the *hkl* peaks of disordered or interstratified *cv/tv* structures.

Identify the unit cell type.

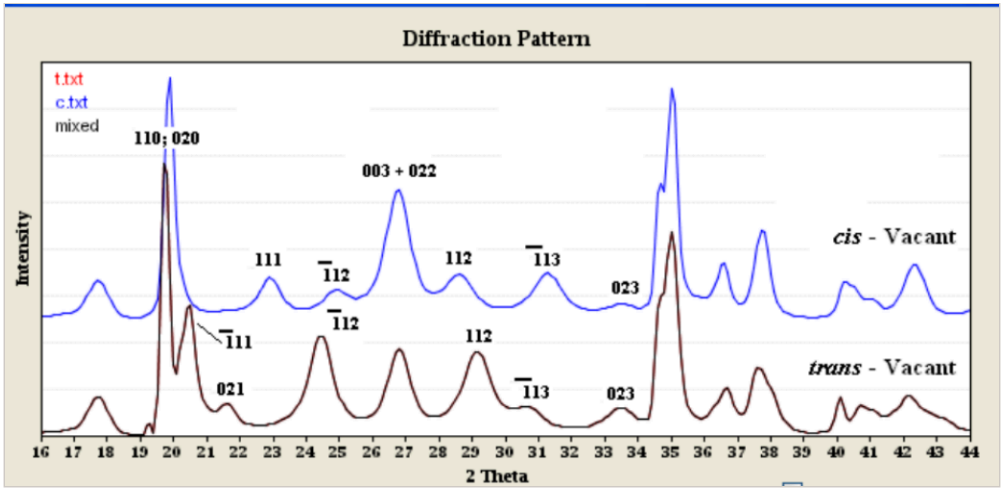


Figure 9. Patterns of slightly disordered (P_0 = 0.8) 1M cis-vacant (top) and trans-vacant (bottom) structures, with reflections labeled.

- The relative heights and positions of the 02*l*; 11*l* ($k \neq 3n$) reflections between 21 and 34° 2θ distinguish *cv* from *tv*.
- The composite 020; 110 peak near 19.9° sits at different positions (Drits et al., 1993): *tv 1M* gives a strong 020 at d = 4.50 Å and a weak 110 at 4.44 Å, while *cv 1M* gives a weak 020 and a strong 110 at 4.46 Å. The difference disappears with strong rotational disorder.
- The $k = 3n$ reflections between 34 and 39° differ because the *tv* monoclinic angle is farther from the ideal orthohexagonal value, which splits the apparent pair between 36 and 39° into four peaks. Disorder reduces this.
- *cv* is best recognized by four 11*l* reflections of about equal intensity. If a pattern looks like *tv 1M* or *1Md* but shows even a subtle maximum near 23° (the 111), the structure contains a significant proportion of *cv* cells. It takes a lot of *cv* to produce a visible 111; small amounts only weaken the *tv* $\bar{1}12$ and 112 peaks.

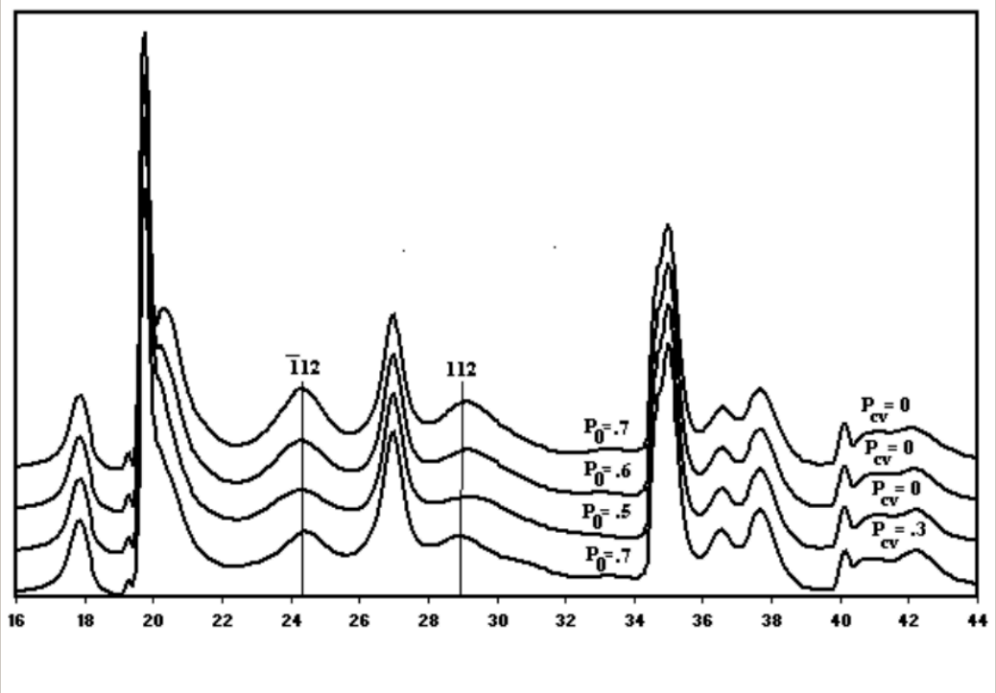


Figure 10. The effects of small amounts of cv interstratification on the tv 1Md pattern.

In this figure the lowest trace is Example III. The three traces above it model it as a disordered *tv* structure with decreasing P_0. Lowering P_0 weakens and broadens the $\bar{1}12$ and 112, but no trace matches both the breadths and the heights of the lowest one. Its 30% *cv* layers give no identifiable 111 at 23°, but weaken the $\bar{1}12$ and 112 without much broadening. The pure *tv* 112 lies at lower angles because β is larger for the *tv 1M* cell, though only a very good pattern would show it. The $\bar{1}12$ position does not change.

Refine in order of speed. Start with the first structure, which is fast, then the second or fourth, depending on the pattern. Adjust P_0 to match the breadths and heights of the 11*l* peaks. n·60° rotations have little effect on the 02*l*; 11*l* reflections, so refine P_0 and P_cv with the faster options, then use the fifth option to bring the 20*l*; 13*l* peaks between 34 and 39° into line. More n·60° rotations move the two reflections between 36 and 39° toward each other; with P_0 small and P_{60} large enough they merge into one peak near 37.2° (Sakharov et al., 1990, for glauconite). Finish with small adjustments of P_0 and P_cv. Use a 0.2° step while modeling and 0.1° for the final pattern.

Study the patterns in Reynolds (1993) to learn the effects of each input. Modeling diffraction patterns is a skill, honed under the pressure of needing to know. And save sparingly: if your file organization is like the author's, you will find it easier to calculate a pattern again than to find an old one.

6. Ordered polytypes

The Ordered solution (**Solutions > Ordered**, called Wildfire Poly in the 1993 manual) is like Disordered but has no rotational disorder. That makes it fast enough for very thick crystallites, up to N3 = 50. Its main uses are:

1. Patterns of detrital mica phases, to subtract from a measured pattern or add to a simulated one to model a mixture (section 11).
2. Reference patterns for the polytypes *1M*, *3T*, *2M*$_1$, *2M*$_2$ and *2Or*.
3. Patterns of very thick crystallites that are random interstratifications of any two mica unit cells.

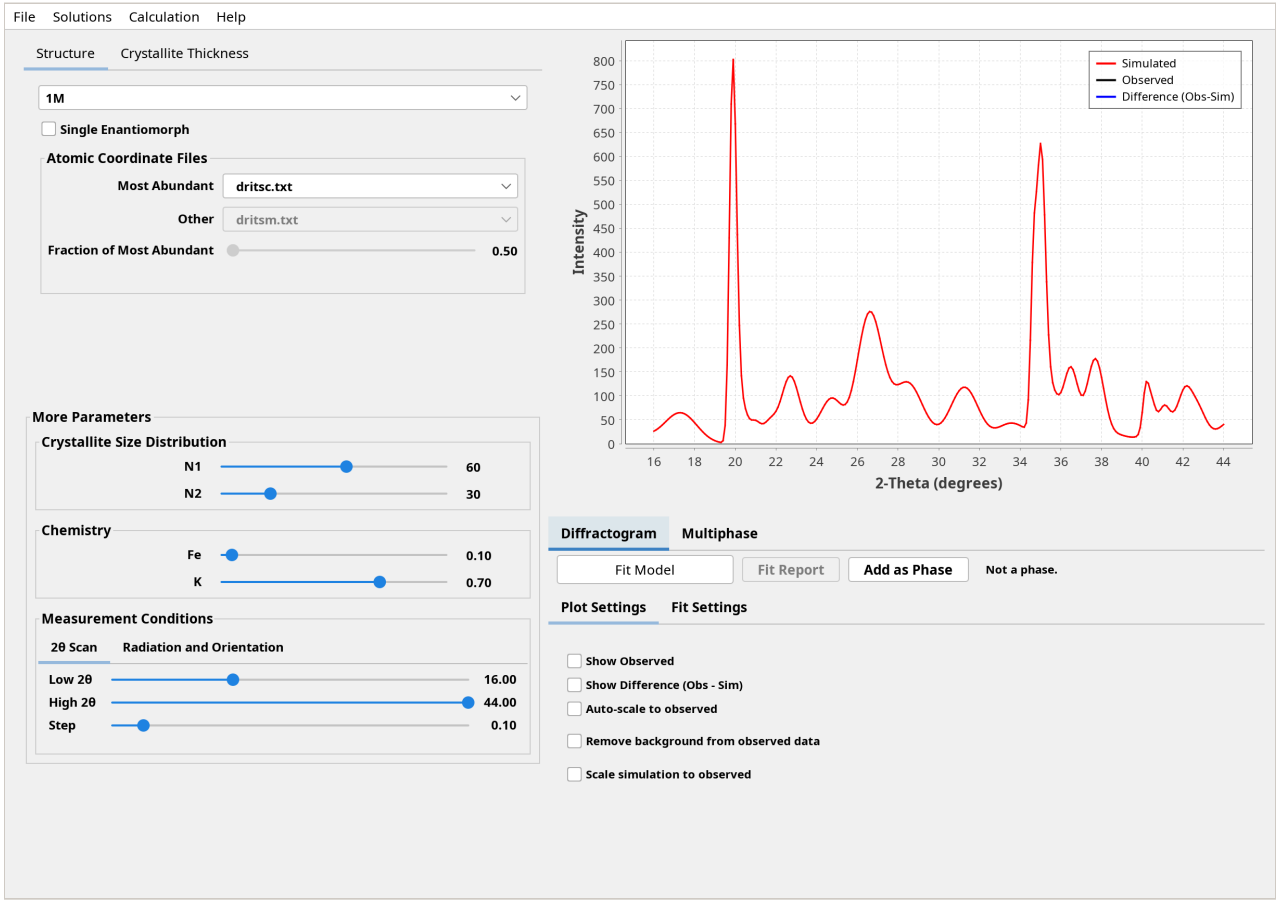


Figure 11. The Ordered solution with the 1M polytype.

Structure tab

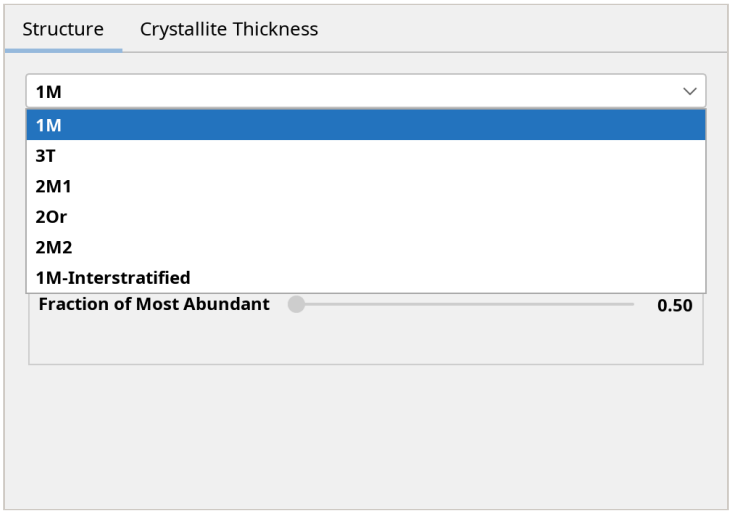


Figure 12. The polytype list.

Control	Range	What it does
Polytype list	1M, 3T, 2M1, 2Or, 2M2, 1M-Interstratified	The stacking sequence
Single Enantiomorph	On or off	For 1*M* with `dritsc.txt` only: calculates one hand of the non-centrosymmetric cis-vacant structure
Most Abundant	Files in `acfiles`	The unit cell; for the ordered polytypes, the only cell
Other	Files in `acfiles`	The second cell, for 1M-Interstratified only
Fraction of Most Abundant	0.50 to 1.00	Share of the most abundant cell, for 1M-Interstratified only; greyed out when the same half cell is chosen twice

At a fraction of 1.00, 1M-Interstratified gives exactly the 1M pattern of the most abundant cell.

The same file twice. Choosing one file as both Most Abundant and Other depends on the kind of cell (section 4):

- A half cell (`dritst.txt`, `dritsm.txt`, `veblen.txt`): both layers are identical, so this is one mineral, the 1M polytype of that cell. The fraction has no effect, so it is greyed out and never fitted, and a note under it reads *Same file twice: 1M of one mineral*.
- The full *cis*-vacant cell (`dritsc.txt`): as in the 1993 program, the second layer is the mirror image of the first, so the two hands (enantiomorphs) of the *cis*-vacant layer are interstratified, and the fraction is the share of one hand. The note reads *Same file twice: its two hands interstratified*.

Crystallite Thickness tab

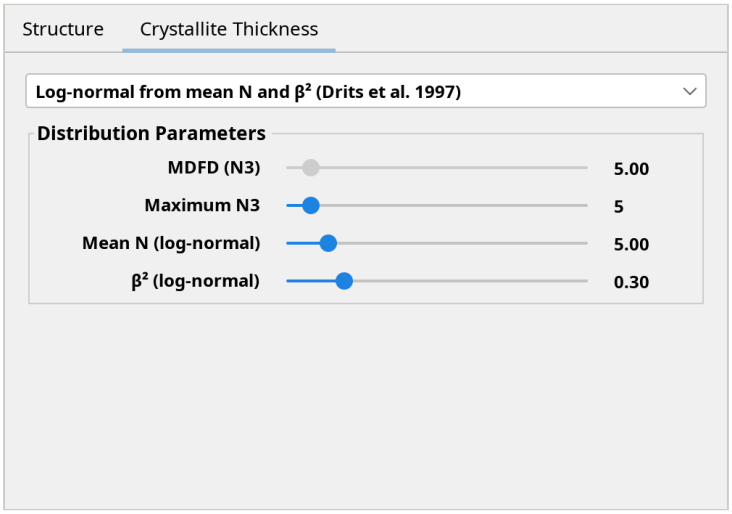


Figure 13. Crystallite Thickness tab of the Ordered solution, with the log-normal option selected.

Option	Inputs
Calculated from defect-free distance and maximum N3	MDFD (N3), the mean defect-free distance, 1.00 to 50.00; Maximum N3, 1 to 50
Log-normal from mean N and β^2 (Drits et al. 1997)	Mean N, 1.0 to 30.0; β^2, 0.01 to 1.50; Maximum N3, 1 to 50

Section 5 (Crystallite Thickness tab) gives the log-normal formula. Set Maximum N3 well above Mean N, since N3 cuts the distribution off.

More Parameters

Control	Range	Default	Meaning
N1, N2	10 to 100	60, 30	Unit cells along X and Y
Fe	0 to 2.00	0.10	Fe atoms per Si_4O_{10}, replacing Al in the two octahedral sites (hence at most 2)
K	0 to 1.00	0.70	K atoms per Si_4O_{10}
OOL Correction Factor	1.00 to 10.00	1.00	Multiplies the 00*l* (basal) intensity relative to the *hkl* intensity
Dollase Factor	0.50 to 1.00	1.00	Preferred orientation (section 4)

The scan runs from 2.0 to at most 44.0° 2θ, with a default of 16 to 44°. As in the 1993 program, the upper limit is set by the *hk* rods the calculation includes: beyond 44° their contributions would be missing.

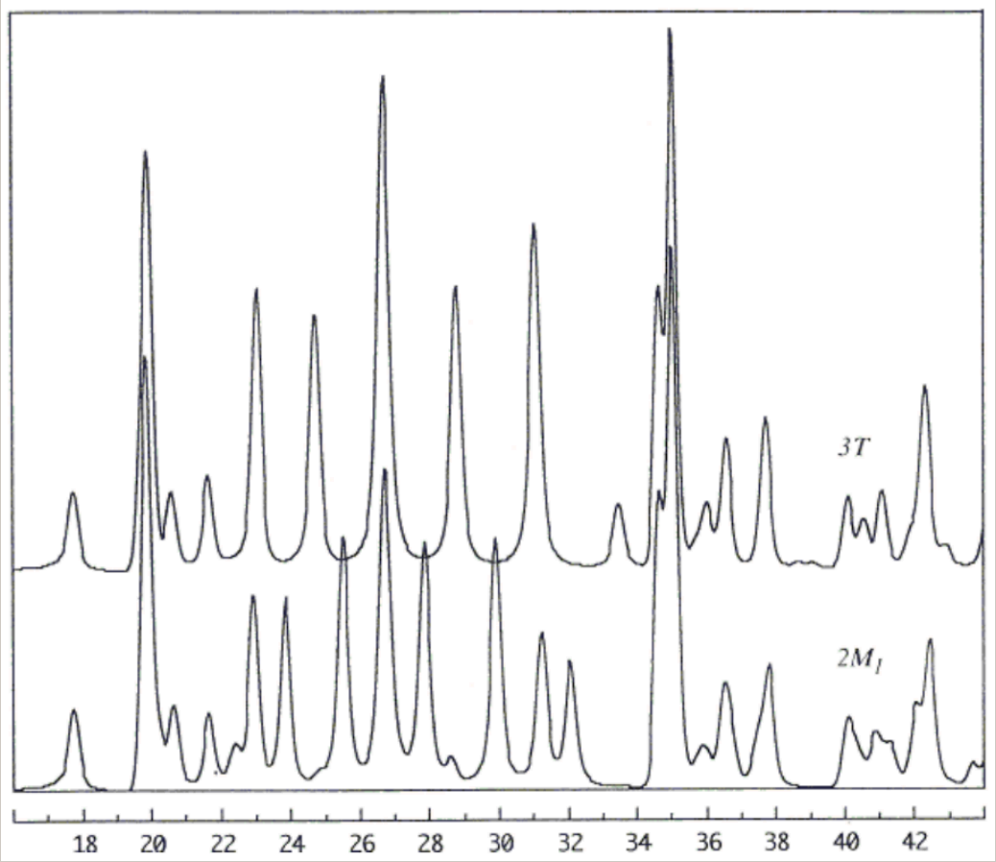


Figure 14. Calculated patterns of the 3T (top) and $2M_1$ (bottom) polytypes.

7. Chlorite

The Chlorite solution (**Solutions > Chlorite**) calculates powder patterns of chlorite polytypes, either one polytype or a random or ordered interstratification of two. The 1993 manual did not cover it, so this section is written from the program itself.

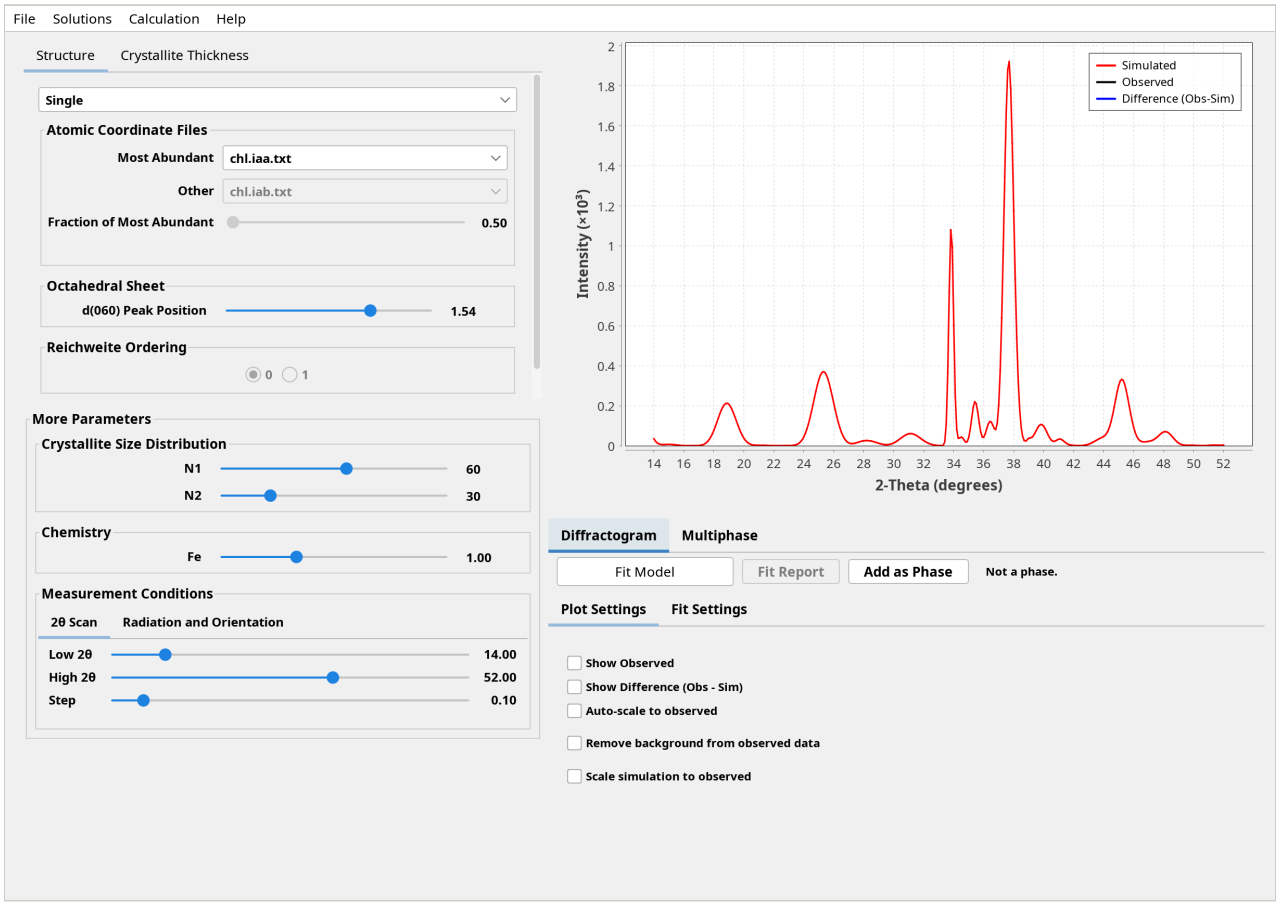


Figure 15. The Chlorite solution with a single polytype.

Structure tab

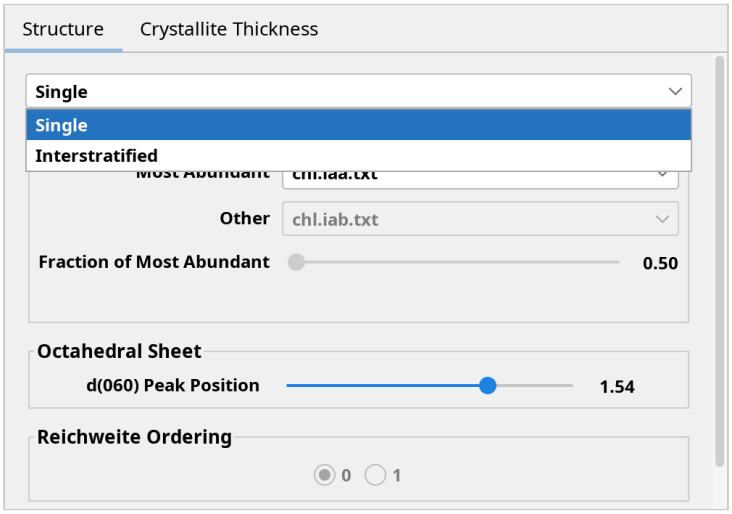


Figure 16. Single or Interstratified structure.

Control	Range	Default	What it does
Single / Interstratified	List	Single	One polytype, or two interstratified
Most Abundant	Files in `chlorite_acfiles`	`chl.iaa.txt`	The polytype, or the more abundant of two
Other	Files in `chlorite_acfiles`	`chl.iab.txt`	The second polytype, Interstratified only
Fraction of Most Abundant	0.50 to 1.00	0.50	Share of the most abundant polytype, Interstratified only; greyed out when the same file is chosen twice
d(060) Peak Position	1.47 to 1.57 Å	1.54	Sets the *b* dimension of both cells, $b = 6 \times$ d(060)
Reichweite Ordering	0 or 1	0	Random (0) or nearest-neighbor ordered (1) interstratification, Interstratified only; greyed out when the same file is chosen twice

The supplied coordinate files, `chl.iaa.txt`, `chl.iab.txt`, `chl.iba.txt`, `chl.ibb.txt` and `chl.iib.txt`, describe chlorite polytypes named for the layer types of Bailey; their first lines give *a*, *b*, *c* and β in the same format as the mica files (section 4).

Which polytypes can be interstratified. The interstratified calculation holds the interlayer shifts for every ordered pair of `chl.iaa.txt`, `chl.iab.txt`, `chl.iba.txt` and `chl.ibb.txt` (12 pairs). Any other pair, including any pair with `chl.iib.txt`, shows *Incompatible Atomic Coordinates!* and is not calculated. Choosing the same file twice is one polytype: it is calculated as Single, the fraction and Reichweite are greyed out, and a note reads *Same file twice: calculated as Single*.

Crystallite Thickness tab

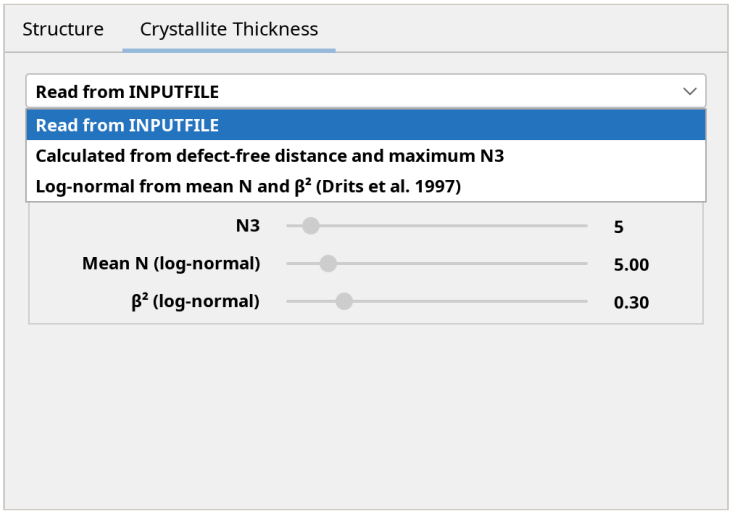


Figure 17. The three thickness options.

Option	Inputs
Read from INPUTFILE	`chlorite_inputfile.txt` (section 12). The supplied file gives crystallites of 2 to 6 layers, mostly 3
Calculated from defect-free distance and maximum N3	Mean Defect-Free Distance, 1.00 to 25.00; N3, 1 to 50
Log-normal from mean N and β^2 (Drits et al. 1997)	Mean N, 1.0 to 30.0; β^2, 0.01 to 1.50; N3, 1 to 50 (section 5)

More Parameters

Control	Range	Default	Meaning
N1, N2	10 to 100	60, 30	Unit cells along X and Y
Fe	0 to 3.00	1.00	Fe atoms replacing Mg in the three octahedral sites (in a coordinate file with Al octahedral sites, at most 2 of them replace Al)
OOL Correction Factor	1.00 to 10.00	1.00	Multiplies the 00*l* (basal) intensity relative to the *hkl* intensity
Dollase Factor	0.50 to 1.00	1.00	Preferred orientation (section 4)

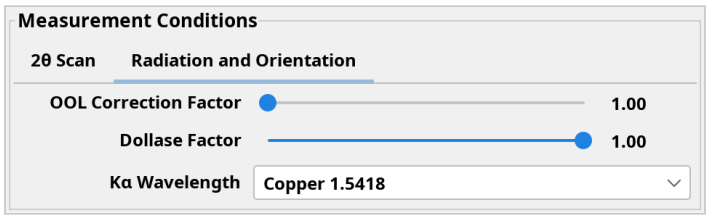


Figure 18. Radiation and Orientation tab with the OOL Correction Factor.

The scan runs from 2.0 to 82.0° 2θ, with a default of 14 to 52°.

8. Peak Intensities Calculator

The Peak Calculator (**Solutions > Peak Calculator**, the Intensity tool of the 1993 manual) gives the position and intensity of any single *hkl* reflection from infinitely thick crystals, for Cu Kα radiation. It suits any space group with symmetry *C*2 or higher. Use it to index measured *1M* mica patterns, to predict peak intensities and positions, and to see quickly how Fe and K change the intensities. The results will not agree exactly with full WildFire patterns, because of the difficulty of separating peaks from background to get accurate integrated areas.

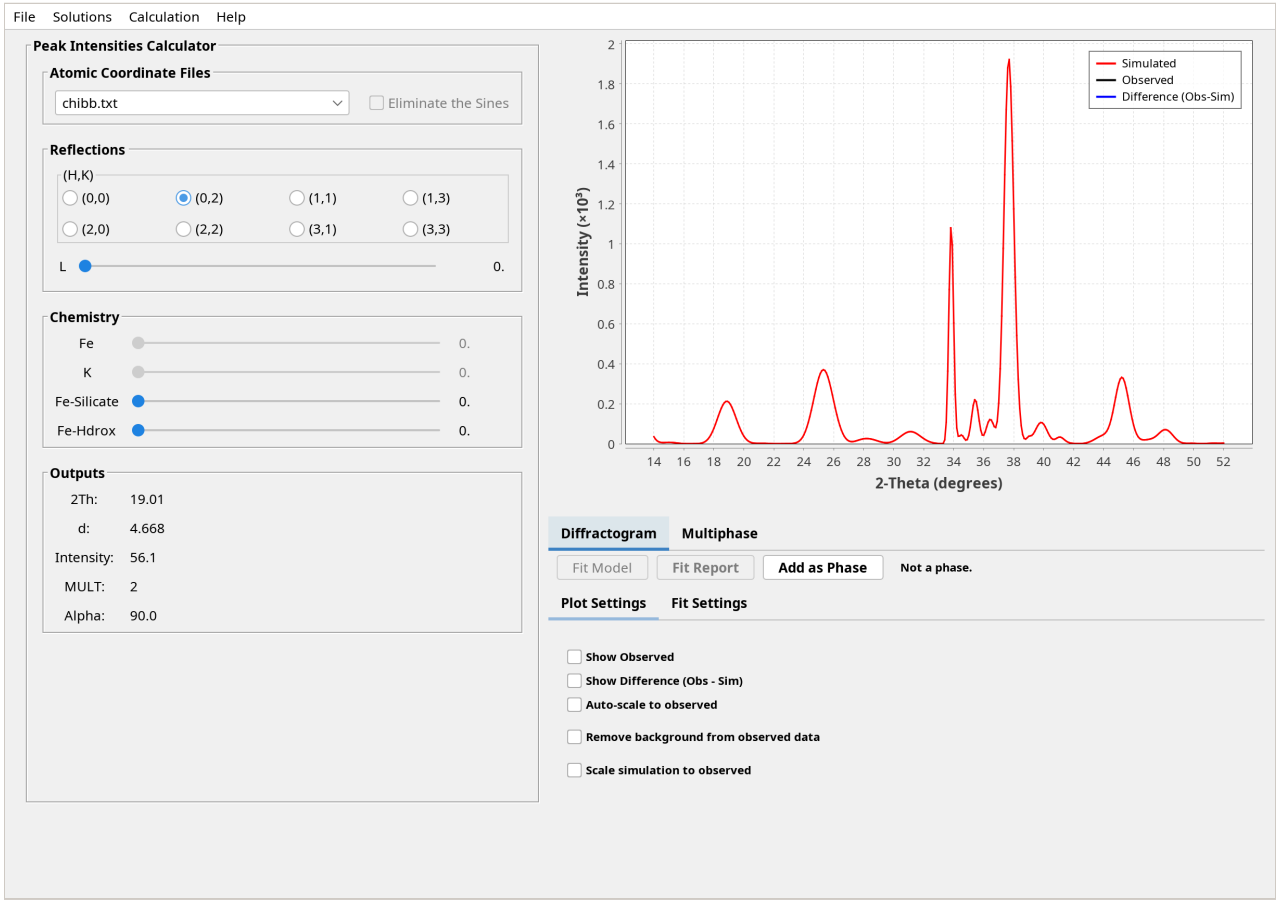


Figure 19. The Peak Intensities Calculator.

The calculator replaces the model panel on the left; the plot keeps showing the last pattern calculated, and there is no fit for this solution. Results update as soon as you change any input; there is no Compute button.

Control	Range	What it does
Atomic Coordinate Files	Files in `intensities_acfiles`	The structure
Eliminate the Sines	On or off	Enabled only for the *cis*-vacant file (`dritscmon.txt`)

Control	Range	What it does
(H,K)	(0,0), (0,2), (1,1), (1,3), (2,0), (2,2), (3,1), (3,3)	The *h* and *k* indices
L	0 to 10	The *l* index; set it to a whole number
Fe, K	0 to 1.00	Fe and K per Si_4O_{10}, for mica files
Fe-Silicate, Fe-Hdrox	0 to 3.00	Fe in the silicate and hydroxide octahedral sheets, for chlorite files

The coordinate files here are not the same as the WildFire files of section 4: their X coordinates are in monoclinic space, not orthogonal space. Mica files are recognized by the K atom they contain, which enables Fe and K; chlorite files enable Fe-Silicate and FeHdrox instead.

Tick **Eliminate the Sines** to drop the sine terms from the structure factor, which is what you will normally want. Leave it clear only to study a single enantiomorph of the *cis*-vacant *1M* structure.

Outputs

Output	Meaning
2Th	The 2θ of the reflection, in degrees
d	Its d-spacing, in Å
Intensity	Relative intensity, on a scale to roughly 100
MULT	Multiplicity, *m*
Alpha	The angle in degrees between the normal to the diffracting plane *hkl* and the normal to (001)

Intensity is calculated as

$$I = \frac{1 + \cos^2 2\theta}{\sin\theta \, \sin 2\theta} \, m \, |F(hkl)|^2$$

where the trigonometric term is the random-powder Lorentz-polarization factor and F is the structure factor.

Alpha helps you think through the effect of preferred orientation on any reflection: orientation strengthens planes with small Alpha and weakens those with large Alpha.

9. Scan, radiation and measured data

Measurement Conditions

Every solution except the Peak Calculator has a **Measurement Conditions** box with two tabs. **2θ Scan** sets the calculated range. Low and High move in steps of 0.01°; Step runs from 0.01 to 1.00°. Calculation time grows with the number of steps: model with 0.2°, keep 0.1° for the final pattern, and use finer steps only to detail one reflection.

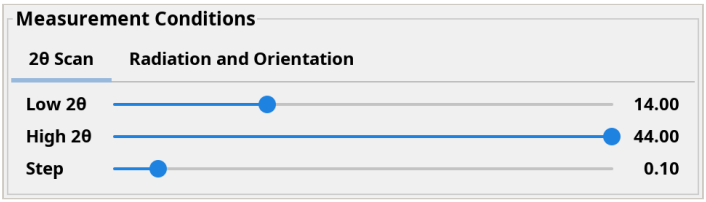


Figure 20. 2θ Scan tab of the Disordered solution.

Solution	Low 2θ	High 2θ	Default
Disordered	2.00 to 41.00	3.00 to 44.00	14 to 44, step 0.10
Ordered	2.00 to 43.00	3.00 to 44.00	16 to 44, step 0.10
Chlorite	2.00 to 81.00	3.00 to 82.00	14 to 52, step 0.10

Radiation and Orientation holds the Dollase Factor (0.50 to 1.00; section 4) and the Kα Wavelength, Copper 1.5418 Å. Copper is the only choice, as in the 1993 programs: the Fe scattering factor includes a dispersion correction that is correct only for copper radiation. Ordered and Chlorite also have the OOL Correction Factor here (sections 6 and 7).

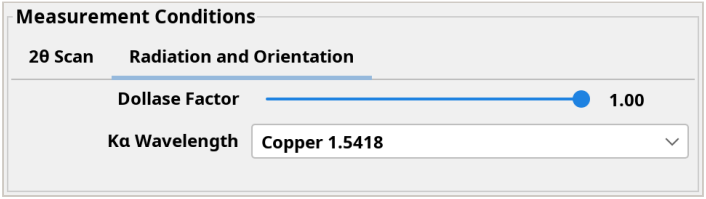


Figure 21. Radiation and Orientation tab of the Disordered solution.

Loading a measured pattern

Choose **File > Input Experimental Curve...** and pick the file. The file must hold two columns, 2θ and intensity, separated by spaces, tabs or a comma, one point per line. Every non-blank line must contain exactly two numbers, so delete any header lines first. It needs at least three points, with 2θ increasing. The dialog lists .txt, .dat and .csv files.

On loading, Low, High and Step of all three solutions are set to match the measured pattern, as far as each solution's range allows; they are not locked. The pattern is trimmed to the current scan range for display and fitting, and stays loaded across solutions. **File > Close Experimental Curve** unloads it and clears the Plot Settings boxes that need it.

Steps the Step slider cannot show. Step moves in hundredths of a degree. When the measured pattern's step is not a whole number of hundredths (0.0167° or 0.005°, for example), WildFire linearly interpolates the measured pattern onto the scan points, Low 2θ plus whole multiples of Step, so that every measured point used falls on a calculated one. This is done again whenever Low or Step changes. The observed curve, the difference curve, auto-scaling, the scale factor and every fit then use the interpolated points. With a Step coarser than the measured step, the interpolation reads the measured pattern at each scan point from its two nearest neighbours; it does not average the points in between, so the noise is not smoothed. Choose a Step close to the measured one to use all the data. The file itself, and the pattern saved in a model or session file, keep the measured points.

Intensity scale. The simulated intensities are on the program's own relative scale (a few hundred to a few thousand), while a measured pattern may have tens of thousands of counts. Tick **Scale simulation to observed** on the Plot Settings tab (below) to multiply the simulated pattern by the factor that best matches the measured one; without it, the overlay, the difference curve and any fit are dominated by the scale mismatch.

Plot Settings

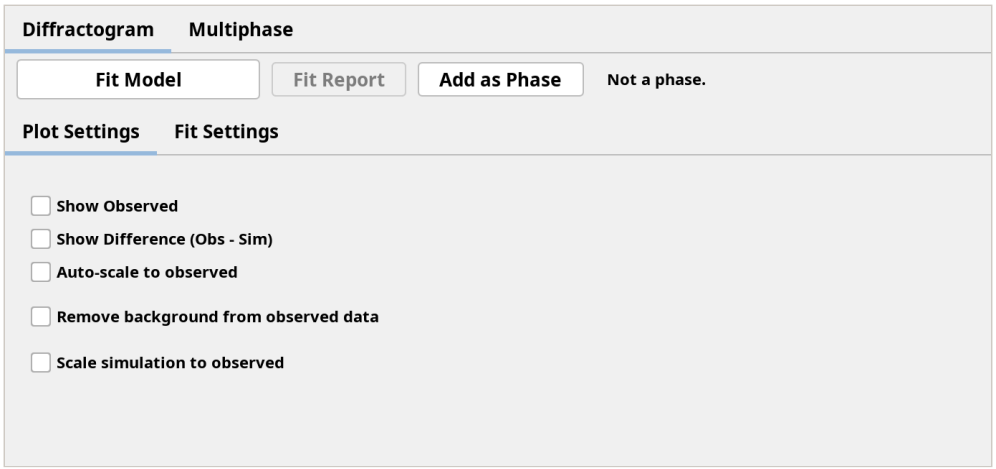


Figure 22. Plot Settings tab, with the Scale simulation to observed check box.

Check box	What it does
Show Observed	Draws the measured pattern in black
Show Difference (Obs - Sim)	Draws measured minus simulated in blue, at the measured 2θ values (or the interpolated ones, above), with the simulation interpolated between its own steps
Auto-scale to observed	Sets the intensity axis to the range of the measured pattern, plus 5%
Remove background from observed data	Subtracts a background estimated by the SNIP peak-clipping method from the displayed measured pattern; values below zero are set to zero
Scale simulation to observed	Multiplies the simulated pattern by the least-squares factor $k = \Sigma(obs \times sim) / \Sigma(sim^2)$, taken over the 2θ range both patterns cover; the factor is shown beside the box

The five boxes act on a measured pattern only; if none is loaded, ticking one shows a warning and clears the box. Background removal changes the displayed pattern and the difference curve. The scale factor, Fit Model and the multiphase fits use the measured pattern without background removal.

The scale factor is recalculated every time the pattern is, so it follows the model as you move sliders and during a fit. The scaled pattern is what you see, save with **File > Save Model**, and add as a phase.

10. Fitting one model

In the single-phase view (the **Diffractogram** tab below the plot), **Fit Model** refines the current solution's parameters until the simulated pattern best matches the measured one. Tick the parameters to refine in the **Parameters to Fit** box on the **Fit Settings** tab, then click **Fit Model**. Disordered, Ordered and Chlorite each have their own set of check boxes; the Peak Calculator has none. The **Optimizer Settings** box beside it holds how a fit runs.

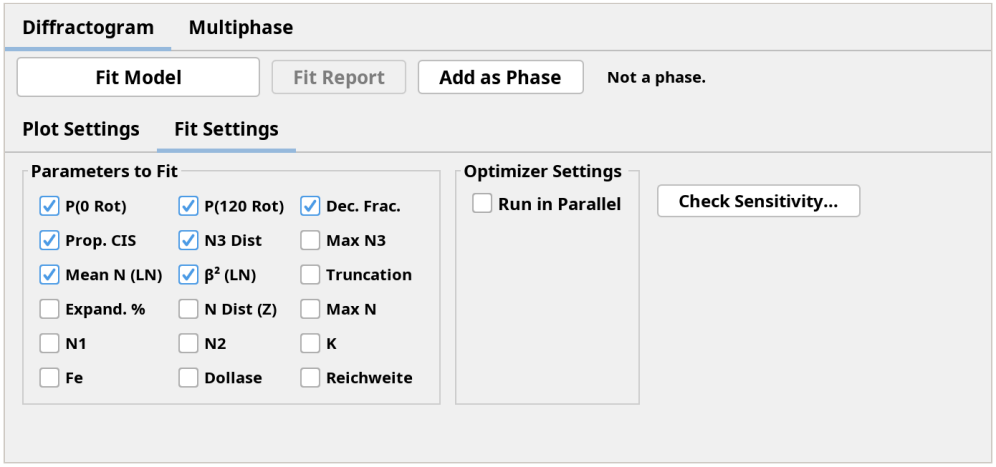


Figure 23. Fit Settings tab of the Disordered solution, with Check Sensitivity... at the right.

Which model is in the panel. A line beside the buttons says whether the model in the main panel is one of the phases (section 11):

- **Phase: *name*, being edited.** You pressed Edit for this phase. Fit here, then press Update on the Phases tab to store the result and the ticked parameters in the phase.
- **Phase: *name*, not being edited.** The main panel holds this phase's model, for example after Add as Phase, Cancel or Fit Models, but a fit here does not change the phase; press Edit first.
- **Not a phase.** The model is not one of the phases, or another solution is shown.

Before you fit

1. Load the measured pattern (**File > Input Experimental Curve...**), and tick **Scale simulation to observed** on the Plot Settings tab (section 9).
2. Choose the structure, thickness and basal options yourself. The fit changes slider values only, not list choices or radio buttons (except Reichweite, below).
3. Set the 2θ scan to the range you want fitted. Only the part of the scan covered by the measured pattern counts.
4. Bring the model close by hand first, and refine few parameters at a time. Each trial recalculates the whole pattern, so a fit of many parameters, or of a slow structure option, can take a long time.

What can be refined

Each check box frees the slider of the same name, within that slider's range.

Solution	Check box	Slider	Ticked at start
Disordered	P(0 Rot)	P(0°)	Yes
Disordered	P(120 Rot)	P(120°)	Yes
Disordered	Dec. Frac.	P(n·60°)	Yes
Disordered	Prop. CIS	Proportion of CIS	Yes
Disordered	N3 Dist	MDFD (N3)	Yes
Disordered	Max N3	N3	No
Disordered	Truncation	Truncate Distribution	No
Disordered	Expand. %	Expandability	No
Disordered	N Dist (Z)	Mean D(z)	No
Disordered	Max N	Maximum N	No
Disordered	N1, N2	N1, N2	No
Disordered	K, Fe, Dollase	K, Fe, Dollase Factor	No
Disordered	Reichweite	Reichweite Ordering (swept, below)	No
Ordered	Abund. Frac.	Fraction of Most Abundant	No
Ordered	N3 Dist (Free)	MDFD (N3)	Yes
Ordered	Max N3	Maximum N3	No
Ordered	N1, N2	N1, N2	Yes
Ordered	Fe, K, OOL Corr., Dollase	Fe, K, OOL Correction Factor, Dollase Factor	No
Chlorite	Abund. Frac.	Fraction of Most Abundant	No
Chlorite	d(060)	d(060) Peak Position	Yes
Chlorite	Defect Dist	Mean Defect-Free Distance	Yes
Chlorite	Max N3	N3	Yes
Chlorite	N1, N2	N1, N2	Yes
Chlorite	Fe, OOL Corr., Dollase	Fe, OOL Correction Factor, Dollase Factor	No
Chlorite	Reichweite	Reichweite Ordering (swept, below)	No
All three	Mean N (LN), β^2 (LN)	Mean N, β^2 (log-normal)	Yes

- In every solution, a ticked parameter whose slider is greyed out for the current choices is skipped. If nothing ticked is active, a message says so. Mean N and β^2 are active only with the log-normal option.
- In Ordered and Chlorite, **Abund. Frac.** starts unticked. Tick it only when fitting an interstratified structure; otherwise its slider is greyed out and the fit skips it. It is also

greyed out when it has no effect: the same half cell chosen twice in Ordered, or the same file chosen twice in Chlorite.
- Whole-number parameters (N1, N2, N3, Maximum N) are rounded to the nearest whole number at each trial.
- In Disordered, **N1, N2** start unticked. The pattern barely changes with them (N1 from 50 to 70 moves it under 0.5% of the strongest peak), so set them by hand.

Reichweite. Reichweite takes only whole values, so it is not refined like the sliders. When Reichweite is ticked, WildFire runs the whole fit once for each allowed value (0, 1 and 3 for Disordered; 0 and 1 for an interstratified chlorite) and keeps the best. It is available only when Reichweite applies: in Disordered, when the counted thickness option or the mixed-layer basal option is chosen; in Chlorite, for Interstratified.

Impossible ordering. Some combinations of Reichweite and expandability cannot exist. Disordered then shows "Nonsense ordering: Reichweite is inconsistent with the proportion of clay type A (PA)." in red on the Reichweite panel and the Fit Settings tab, and the fit treats that trial as a very poor match.

Running a fit

The fit searches within the slider ranges, with every parameter scaled to its slider's range, using the BOBYQA method from Apache Commons Math (at most 2,000 trials). It then finishes on the sliders' own steps: each parameter, and each pair of parameters together, is moved up and down by 8, 4, 2 and finally 1 slider step, keeping any move that lowers the error, until no move helps. The quantity minimized is the sum of squared differences between the simulated pattern and the measured pattern interpolated to the simulated 2θ values. The sliders and plot move only when a trial improves on the best fit so far.

- While a fit runs the **Fit Model** button reads **Cancel**. Click it to stop; WildFire then sets the best values found so far and says so.
- When the fit ends, the uncertainties are estimated for the Fit Report (below); the button reads **Uncertainties…** for those few seconds. A message then gives the final sum of squared error, and **Show Fit Report** in it opens the report. The panel keeps the best values.

Run in Parallel, in the Optimizer Settings box on the Fit Settings tab, spreads each calculation over the computer's processor cores: both ordinary recalculations and every trial of a fit. On a multi-core machine this makes the pattern respond faster and fits finish sooner. It starts unticked; tick it unless you are checking a result against the one-core calculation.

With **Scale simulation to observed** ticked, the scale factor is recalculated at every trial, so the fit matches the shape of the pattern rather than its overall intensity, and the reported error is for the scaled pattern.

Judge the result by eye as well as by the number. Check the difference curve, and make sure the refined values make physical sense: the fit can reach a smaller error with an unrealistic combination, such as a poor Dollase factor standing in for a wrong structure.

Example. The three figures below show a fit on a test pattern. WildFire calculated a Disordered pattern (n·120° disorder, the default structure) with N1 = 45 and N2 = 30, from 16 to 44° 2θ in steps of 0.05°, added a flat background of 20 counts and counting noise, and loaded it as the measured pattern. N1 was then set back to 60, Scale simulation to observed was ticked, and only N1 and N2 were ticked on Fit Settings.

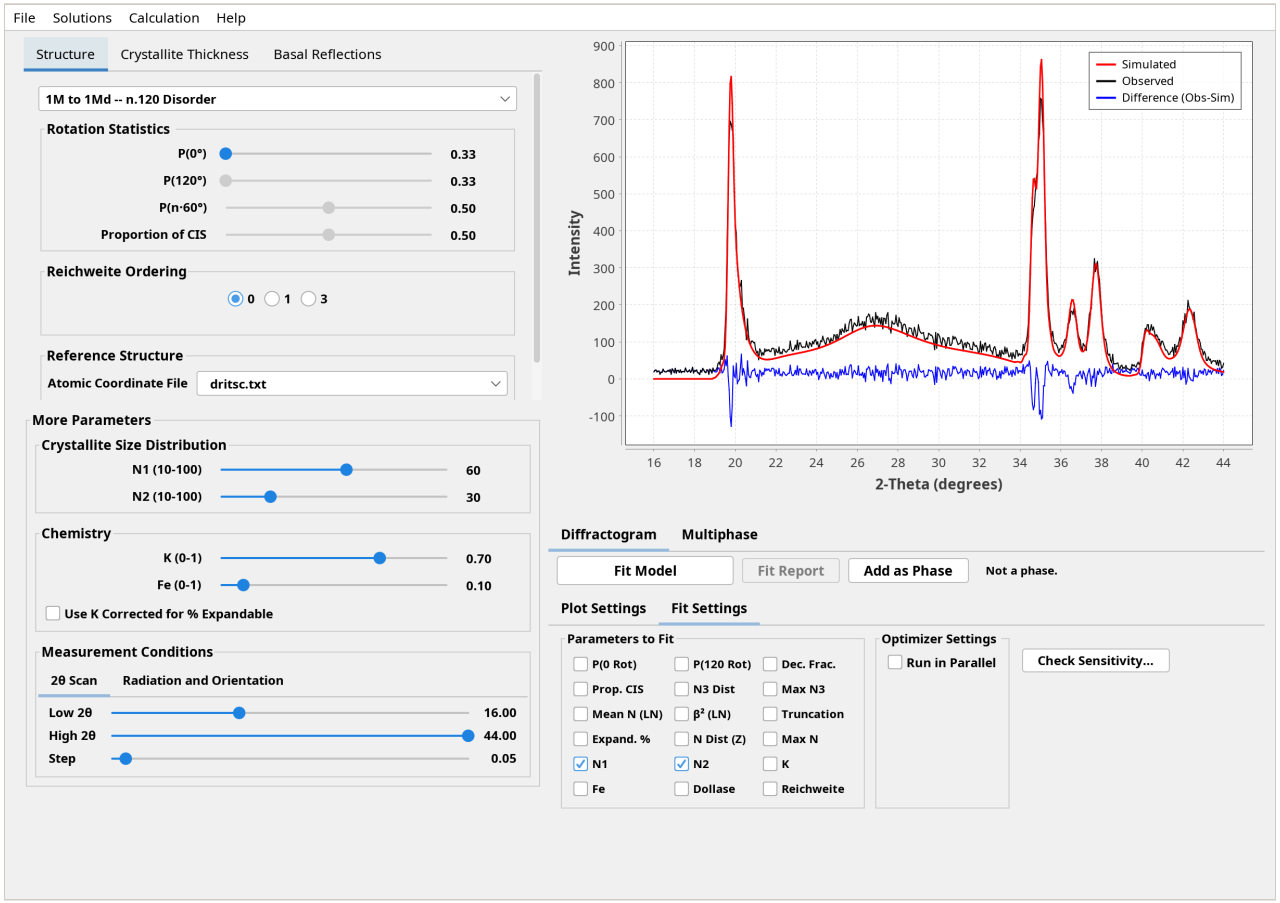


Figure 24. Before Fit Model: N1 = 60 against a pattern made with N1 = 45, with N1 and N2 ticked.

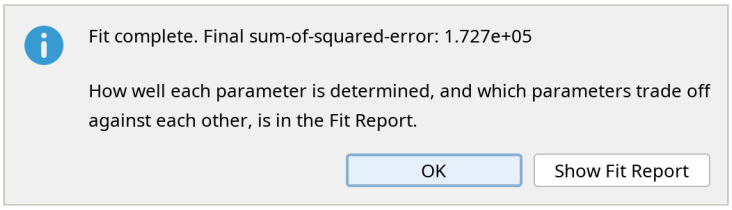


Figure 25. The message at the end of a fit, with Show Fit Report.

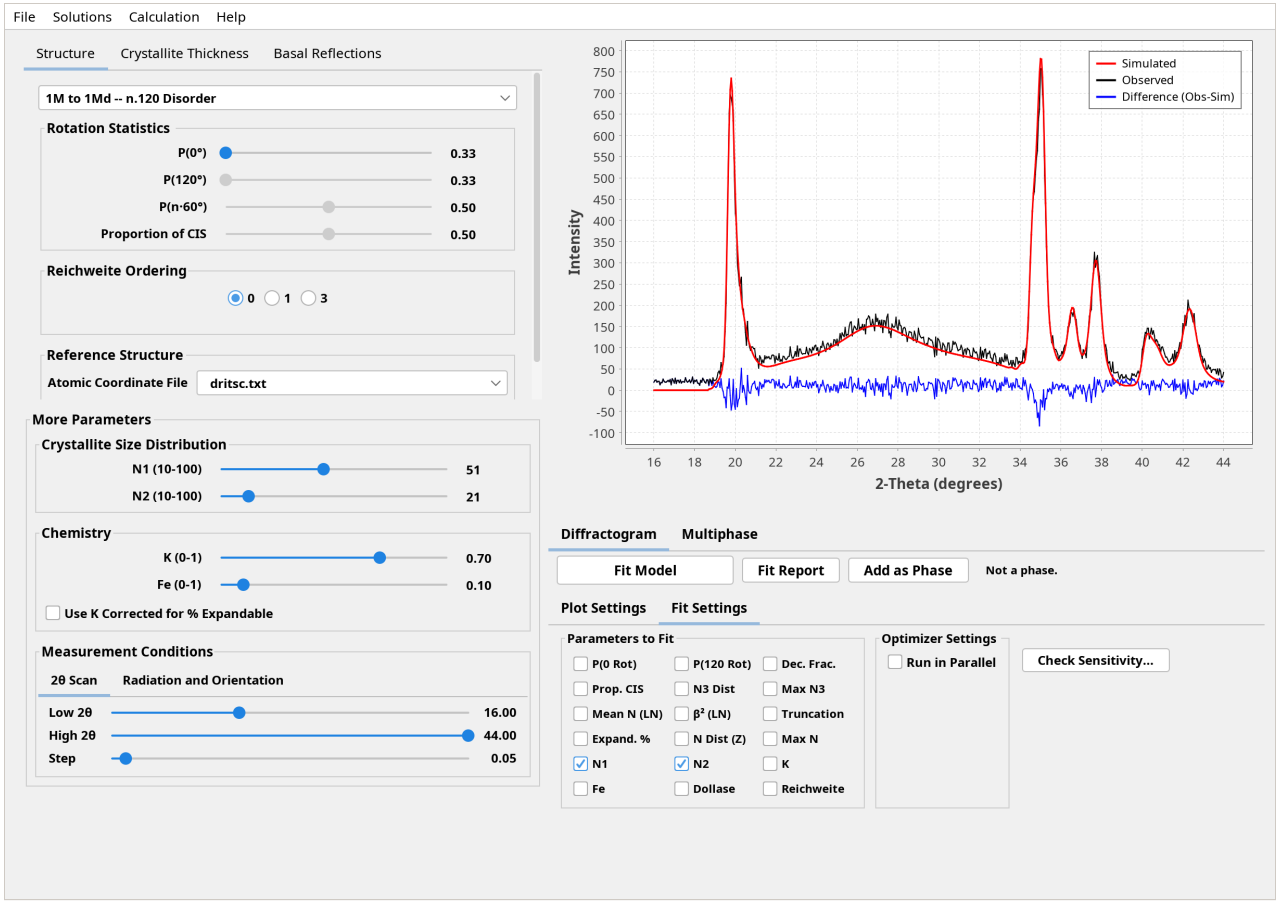


Figure 26. After Fit Model.

The fit ended at N1 = 51 and N2 = 21, not at 45 and 30. The calculated pattern is close to the measured one, but the difference curve still shows misfits near 20 and 34° 2θ. N1 and N2 change the pattern in small, uneven steps, so the fit stopped in a nearby dip of the error surface. The reduced chi-square of 4.7 in the Fit Report (below), well above the 1 that counting noise alone would give, is the sign that the model still misses something. This is why N1 and N2 start unticked in Disordered: set them by hand unless you have a reason to fit them.

The Fit Report

A fit finds the best values; the Fit Report says how well the measured pattern pins each of them down. It opens from **Show Fit Report** at the end of a fit, or at any time from **Fit Report** beside Fit Model, which is greyed out until the first fit. The window can stay open beside the main window and always shows the report of the most recent Fit Model, in any solution. The multiphase fits have a report of their own (section 11). **Copy** puts the whole report on the clipboard, **Save...** writes it to a `.txt` file, and **Close** closes the window.

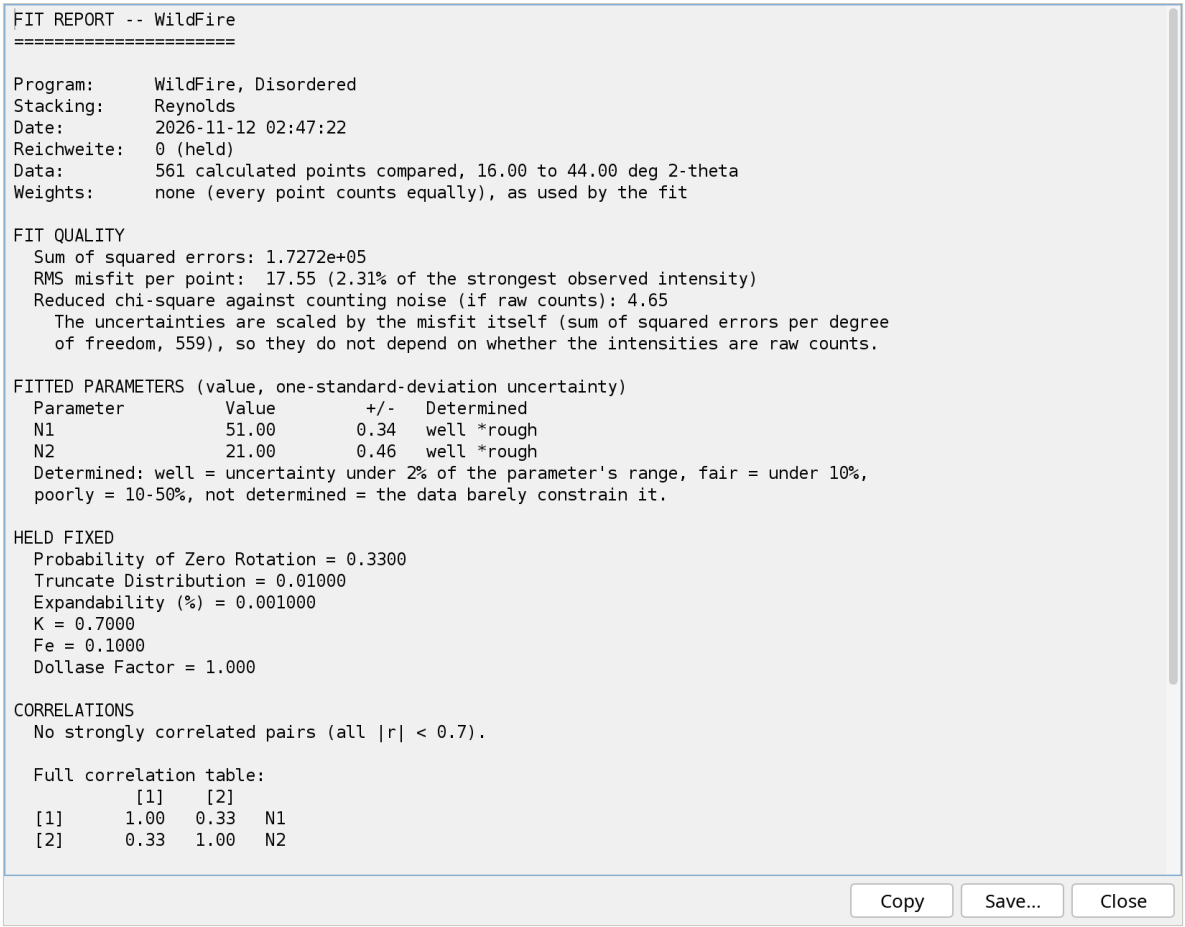


Figure 27. The Fit Report for the example above.

Part	What it says
Heading	Solution, stacking method, date, Reichweite (Disordered and Chlorite), the points and 2θ range compared, and the weighting (none: every point counts equally, as in the fit)
Fit quality	The sum of squared errors; the RMS misfit per point, also as a percentage of the strongest measured intensity; and a reduced chi-square against counting noise (below)
Fitted parameters	Each fitted value with its one-standard-deviation uncertainty (±) and how well it is determined, with flags
Held fixed	The active parameters of the solution that were not ticked, with their values
Correlations	Pairs of parameters that trade off against each other, then the full correlation table

Determined. The uncertainty is compared with the slider's range: **well** means it is under 2 % of the range, **fair** under 10 %, **poorly** 10–50 %, and **not determined** means the pattern barely constrains it. ***limit** flags a value at the end of its slider, where the best value may lie beyond the range; ***rough** flags an uneven error surface near the value (the slopes on either side differ), where the uncertainty may understate the real spread. Each parameter moves in whole slider steps, so an uncertainty smaller than one step means the pattern pins it to within a step.

Reduced chi-square against counting noise divides each squared difference by the measured intensity (the variance of a raw count) and the sum by the degrees of freedom. If the intensities are raw counts, a value near 1 means the misfit is about what counting noise alone would give; well above 1 means the model leaves a systematic misfit. The uncertainties themselves are scaled by the fit's own error per degree of freedom, so they do not depend on whether the intensities are raw counts.

Correlations. A correlation near +1 or −1 means two parameters can compensate each other: changing both together leaves the pattern almost unchanged, so neither is well determined on its own. Strong pairs (|r| ≥ 0.9) and moderate ones (0.7–0.9) are listed first. Fixing one member of a strong pair, from other knowledge, usually sharpens the other.

How it is calculated. After the fit, the pattern is calculated with each fitted parameter moved up and down by a whole number of slider steps (about 1 % of the slider's range), two patterns per parameter, which gives how the pattern changes with each parameter, J. The plot and sliders are put straight back after every trial. With s^2 the final sum of squared errors per degree of freedom,

$$\mathrm{cov} = s^2 \left(J^{\mathsf{T}} J\right)^{-1}, \qquad \sigma_i = \sqrt{\mathrm{cov}_{ii}}, \qquad r_{ij} = \frac{\mathrm{cov}_{ij}}{\sigma_i \, \sigma_j}$$

These are the standard linearized least-squares estimates. They describe the error surface near the answer found and assume the misfit behaves like random noise; they cannot tell whether a different, distant set of values fits as well. The example above is a case in point: around N1 = 51 and N2 = 21 the error surface is steep, so the report calls both well determined (with the *rough flag on both), yet the true values were 45 and 30. A small uncertainty means the answer is sharply defined where it is, not that it is the right answer; the reduced chi-square and the difference curve tell you whether the model fits.

Checking sensitivity: which parameters to fit

A pattern cannot pin down every parameter at once. Some barely change it, and some change it in the same way as another, so the two can trade off without changing the fit. Fitting them makes a fit slower and its results less certain. The **Check Sensitivity…** button, to the right of the boxes on the Fit Settings tab (Figure 23), tests each parameter of the current solution in a few seconds and, in the **Suggest** column of its report, recommends which ones to tick. It needs a measured pattern. It does not fit anything or change the model.

The check moves each slider up and down by about 5 % of its range (in whole slider steps), holding the others, recalculates the pattern exactly as Fit Model does (scaled to the measured pattern when Scale simulation to observed is ticked), and measures how much the match changes. The plot and sliders are put straight back after every trial. Parameters whose sliders are greyed out for the current choices are listed as **not used**. While it runs, the **Check Sensitivity…** button shows the progress; press the button again to stop. The report opens in a window of its own (Figure 28).

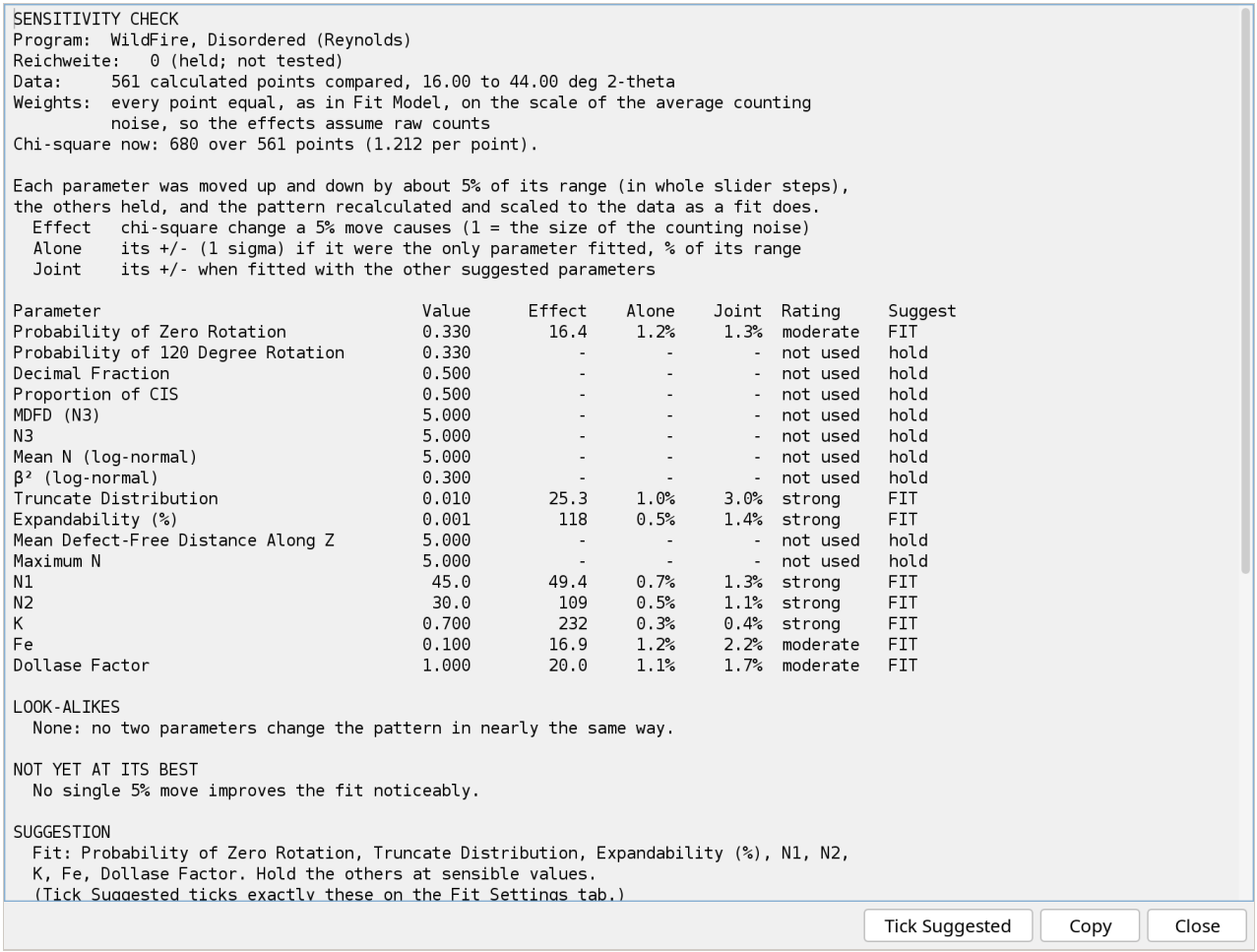


Figure 28. The sensitivity report for a Disordered test pattern.

Column	What it says
Effect	How much a 5 % move changes the match, on the scale of the counting noise: 1 is about the size of the noise for raw counts, so below 1 the pattern can hardly see the parameter. Fit Model weights every point equally; the check divides by the average measured intensity to put the effect on this scale.
Alone	The parameter's ± (one standard deviation) if it were the only one fitted, as a % of its slider's range
Joint	Its ± when fitted together with the other parameters marked **FIT**. This is the number that matters for a fit, and it is often larger than Alone.
Rating	**strong** (effect 25 or more), **moderate** (1 to 25), **weak** (under 1), **no effect**, or **not used**
Suggest	**FIT** (tick this parameter) or **hold** (leave it unticked at its current value). A * next to **hold** marks a parameter that matters on its own but is not marked **FIT** in the Suggest column; the reason is given below the table.

Look-alikes are pairs whose effects on the pattern are nearly the same (similarity 0.95 or more), such as MDFD (N3) and Maximum N3 in Ordered, or the OOL Correction Factor and the Dollase Factor in Chlorite. The pattern can fix their combined effect but not how it is shared between them, so the Suggest column marks only one of each pair **FIT**.

How the Suggest column is decided. It starts from the strong and moderate parameters, keeps one of each look-alike pair, and then drops parameters one at a time until every one left is determined jointly to within 10 % of its range. When two parameters trade off, the one kept is chosen in this order: the structural parameters first; then the OOL and Dollase factors and the whole-number limits N3, Maximum N3 and Maximum N; then K and Fe, which are often known from chemical analysis. **Not yet at its best** lists any parameter whose 5 % move already improves the match noticeably, a sign that the model is not yet near its best values.

Three buttons sit at the bottom of the report. Press the **Tick Suggested** button to tick, on the Fit Settings tab, every parameter marked **FIT** in the Suggest column and untick all the others (Figure 29); the Reichweite box is left as it is. Press the **Copy** button to put the report on the clipboard, and the **Close** button to close it. Then press the **Fit Model** button as usual.

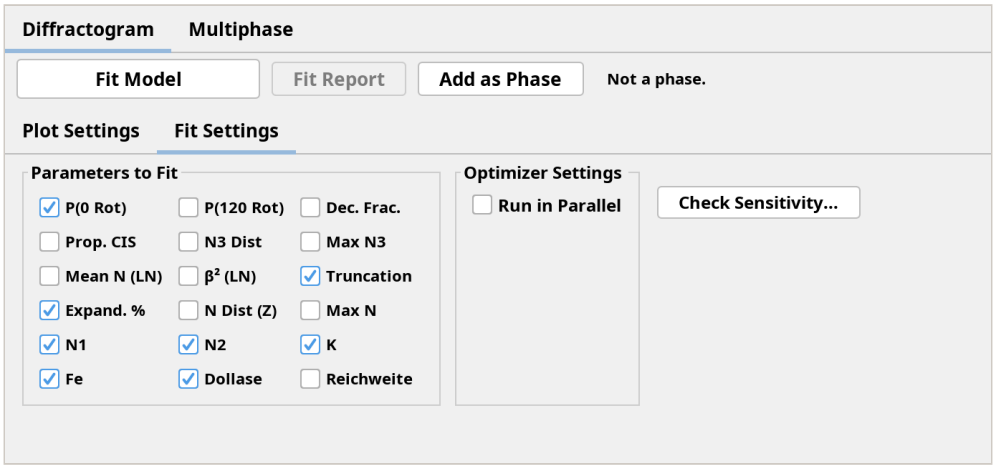


Figure 29. The Fit Settings tab after pressing the Tick Suggested button.

Example. The pattern of the fit example above was calculated again with N1 = 45 and N2 = 30, without the background this time, with counting noise, and the model was left at those values. The check took about 4 seconds. Nine parameters are greyed out for the default options and were not tested. All eight that apply are strong or moderate and determined jointly to within 3 % of their ranges, so all eight are marked **FIT** in the Suggest column, and none is yet off its best value.

Limits. The check is local: it describes the model near its current values, so it is most useful once the model is roughly right, and it is worth running again after a fit. It does not test list choices or radio buttons (structure, polytype, thickness and basal options) or Reichweite. It assumes the intensities are raw counts, and it is not available for the multiphase view.

11. Multiphase patterns

A multiphase pattern models a sample that contains more than one phase: the weighted sum of up to four phases, each with its own model. For example, a disordered illite from the Disordered solution plus a detrital $2M_1$ mica from Ordered, or an illite plus a chlorite. Each phase keeps its full model, so the fit can refine the models as well as the weights, as Newmod III does. Non-clay minerals, such as quartz, feldspars and carbonates, can be added to the sum as reference minerals, with a smooth background (below).

Open the **Multiphase** tab below the plot for the multiphase view. The plot then shows the weighted sum, and the tab holds **Fit Weights**, **Fit Models** and **Fit Report**, with four tabs: Plot Settings (shared with the single-phase view), Fit Settings (each phase's ticks), **Phases**, with one row per phase, and **Minerals**.

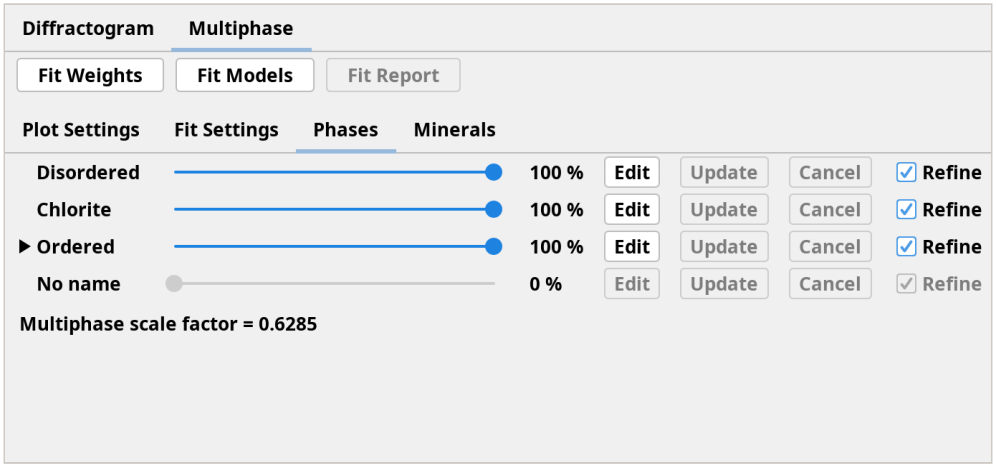


Figure 30. The Phases tab with three phases; the ▶ marks the phase loaded in the main panel.

Building a multiphase pattern

1. Set up the first phase's model in any solution until its pattern looks right.
2. In the single-phase view (the **Diffractogram** tab), click **Add as Phase** and type a short name. If you leave it blank, the solution's name is used. The phase goes into the first row whose weight is 0 %, with its weight at 100 %.
3. Set up the next phase, in the same or another solution, and add it the same way. Up to four rows can be filled.
4. Open the **Multiphase** tab to see the weighted sum in red. The measured pattern (black) and the difference curve (blue) follow the Show Observed, Show Difference and Remove background boxes on the Plot Settings tab, as in the single-phase view.

Each row on the Phases tab has these controls:

Control	What it does
Name	The name you typed. A ▶ marks the phase now loaded in the main panel.

Control	What it does
Weight slider and %	The phase's weight in the sum, 0 to 100 %. Setting it to 0 % removes the phase and frees its row.
Edit	Loads this phase's model into its solution's panel and switches the window to that solution, so you can see or change it. Until you press Update or Cancel, every other phase's buttons, Add as Phase and Fit Models are disabled.
Update	Replaces this phase with the model now in the main panel, keeping its name and weight. Enabled only while this phase is being edited, and ends the edit.
Cancel	Enabled only while this phase is being edited. Abandons the edit: the phase is left unchanged and the window goes back to the solution and settings it showed before Edit.
Refine	Ticked: **Fit Models** refines this phase's model. Unticked: its model is kept as stored. Either way its weight is fitted.

A phase stores its pattern and every setting on its solution's panel, including the coordinate files, the list choices, the sliders and the Fit Settings ticks. Changing the main panel afterwards does not change the phase until you click **Update**.

Each phase's parameters. In the multiphase view, Fit Settings shows one phase's ticks; choose the phase from the **Phase** list at the top. The list shows the check boxes of that phase's own solution. A tick is stored in the phase at once and used by **Fit Models**; no Edit or Update is needed. **Run in Parallel**, in the Optimizer Settings box beside the ticks, sets Run in Parallel for all three solutions at once, so every phase's calculations in **Fit Models** use all processor cores.

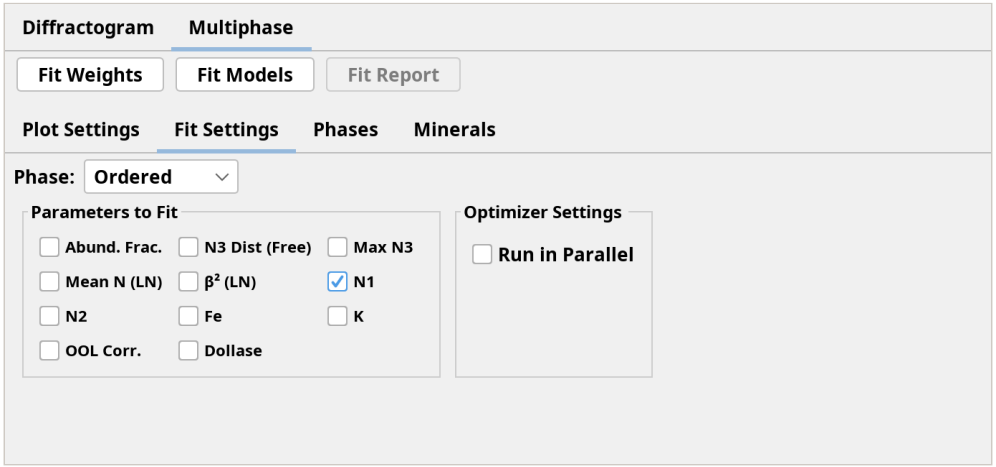


Figure 31. Fit Settings in the multiphase view, with the Ordered phase chosen.

Scale. With **Scale simulation to observed** ticked on the Plot Settings tab, the sum of the phases is multiplied by the factor that best matches the measured pattern. The factor is shown under the rows, and the weights then act as proportions. Without it, the weights are absolute multipliers of the phases' calculated intensities, and the sum is compared with the measured pattern as it is. Tick it when your measured pattern is in counts. Reference minerals and the background are added after the scaling: their weights are in the measured pattern's own units.

The phases may have different 2θ steps and ranges. The sum is formed at the 2θ values of the first phase, with the others interpolated, over the range that all the phases cover.

Fitting a multiphase pattern

Both fit buttons need a measured pattern, and use the measured 2θ values within the range that all the phases cover. Without reference minerals they need at least two phases; with them, one phase is enough, and Fit Weights can also fit minerals alone. Every point counts equally.

Fit Weights finds the weights that best match the measured pattern and moves the sliders to them. Without reference minerals it solves the least-squares problem exactly, so it is instant; each weight stays between 1 % and 100 %. With reference minerals it also fits the minerals' weights and the background, and, for minerals with **Fit** ticked, their peak shifts and widths (below). The phase models are not changed.

Fit Models refines the models of the phases with **Refine** ticked, and fits all the weights as it goes. Fitting the weights adds no time: each refined phase's weight is solved exactly at every trial, and the full set of weights is re-solved after each phase, so the weights of phases that are not refined follow the changing models. For each phase it refines the parameters ticked for that phase on Fit Settings, and sweeps Reichweite if that box was ticked. It works in cycles:

1. With reference minerals, the minerals, their shifts and widths, and the background are fitted first, with the phases as they stand. They are then held while the phases are refined.
2. All phase weights are solved together.
3. The phases are refined one at a time, strongest first. Each is fitted against what the other phases, the minerals and the background leave unexplained, with its own amplitude solved at every trial. The window switches to each phase's solution as it is refined.
4. After each phase, all weights are solved together again.
5. Cycles repeat until a cycle improves the fit by less than 1 %, or four cycles have run.
6. When two or more phases are refined, all their ticked parameters are refined together once more, with the weights solved at every trial. This lets two phases that trade off against each other move together.
7. With reference minerals, the minerals and the background are fitted again, with the final phases.

The status line shows the cycle, the phase and the trial number. Click the button again while it runs to cancel; each phase keeps the best model found before stopping, and the weights are solved again. A summary at the end reports the number of cycles, the sum of squared error before and after, the final weights and, with Scale ticked, the multiphase scale factor. **Show Fit Report** in it opens the Fit Report (below). At the end, the last phase refined is loaded in the main panel and marked ▶.

Example. In the figures below, the measured pattern was made by WildFire from one phase of each solution: the default Disordered, Chlorite and Ordered models with N1 = 40, 45 and 50, scaled to peak heights in the proportions 1 : 2 : 1, with a flat background of 30 counts and counting noise. The three phases were then added with N1 at 60, the weights at 100 %, Scale simulation to observed ticked, Refine ticked for all three and only N1 ticked on each phase's Fit Settings. Before the fit, the difference curve shows misfits at most peaks, largest near 20, 34 and 38° 2θ.

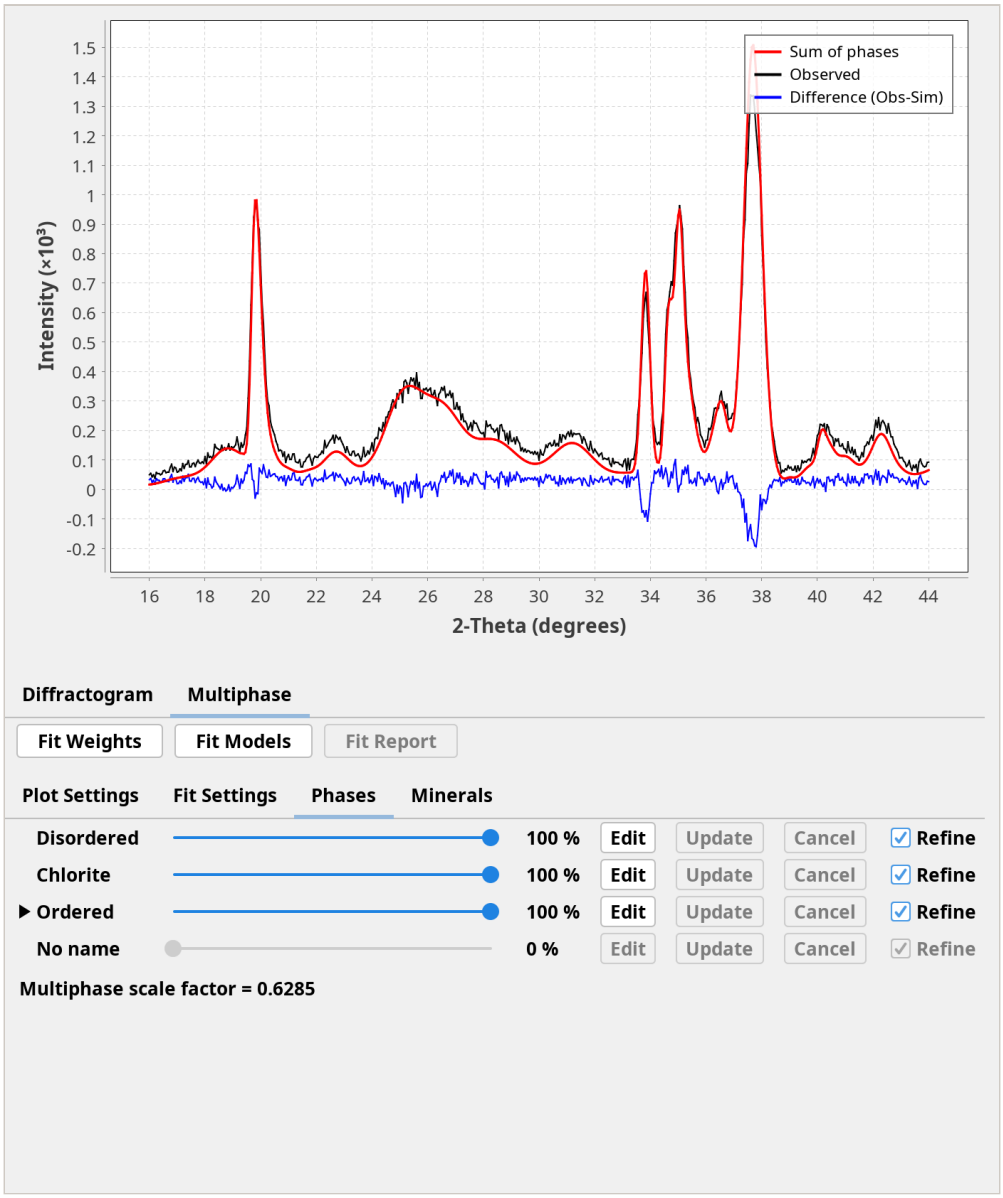


Figure 32. Before the fit: the perturbed phases against the measured pattern.

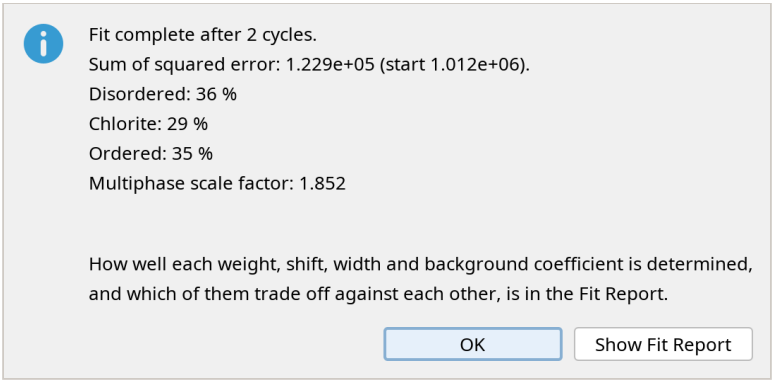


Figure 33. The summary at the end of Fit Models.

Fit Models finished after two cycles, with the sum of squared error down from 1.0×10^{6} to 1.23×10^{5}, close to what the counting noise alone gives (the reduced chi-square in the report is 1.03). The sum now lies on the measured pattern and the difference curve is flat. The weights, 36, 29 and 35 %, are proportions of each phase's calculated intensity, not of peak height, so they need not repeat the 1 : 2 : 1 used to make the pattern. A test like this, which starts from a known answer, is a good way to see how well a set of parameters can be recovered before you fit real data.

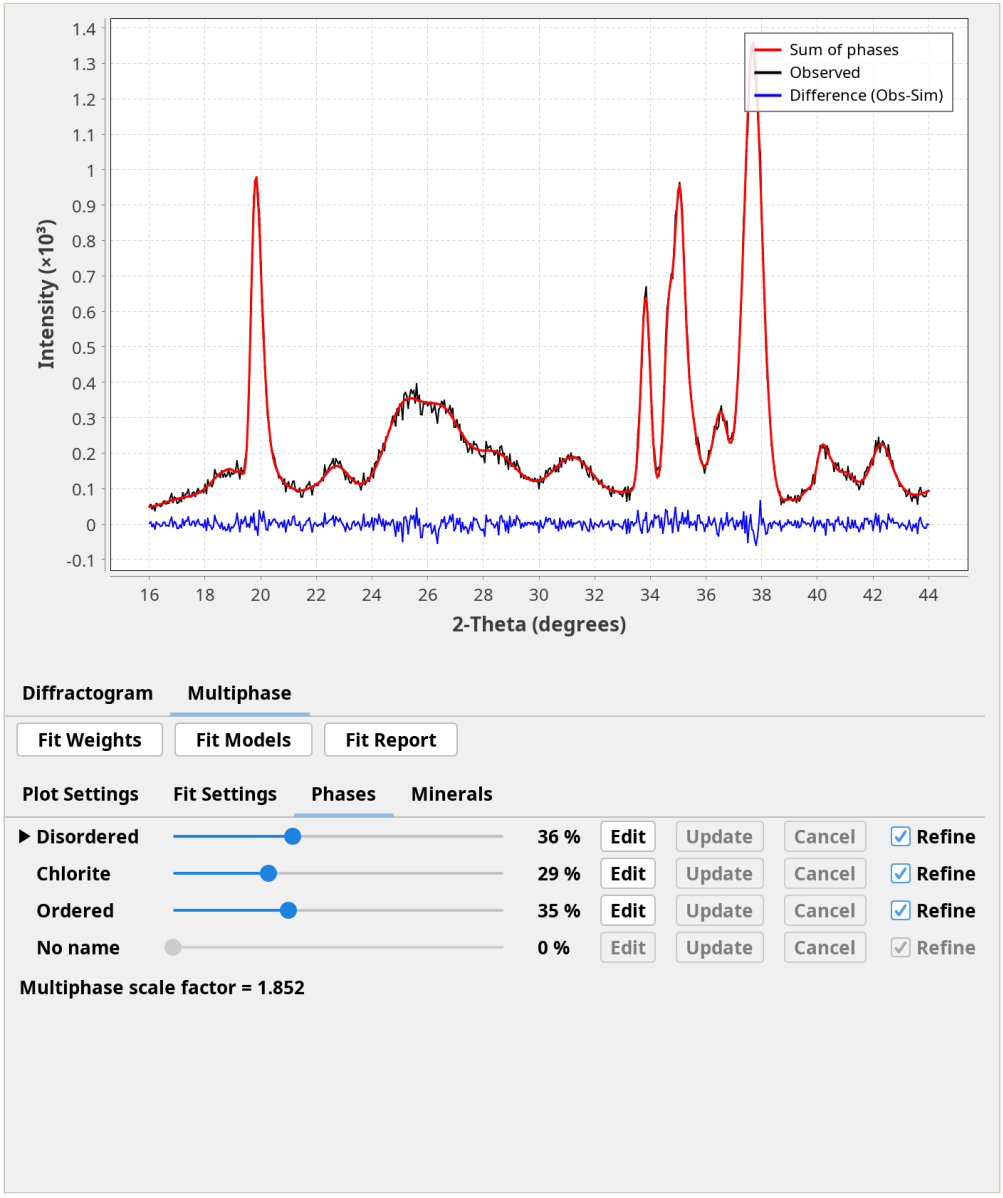


Figure 34. After Fit Models: the refined phases and weights.

The multiphase Fit Report

Fit Weights and Fit Models each publish a Fit Report, like Fit Model's (section 10). It opens from **Show Fit Report** in the summary, or at any time from **Fit Report** on the Multiphase tab, which is greyed out until the first multiphase fit and always shows the most recent one. The single-phase and multiphase reports are kept separately, so a Fit Model does not replace the report of a Fit Models, or the other way round.

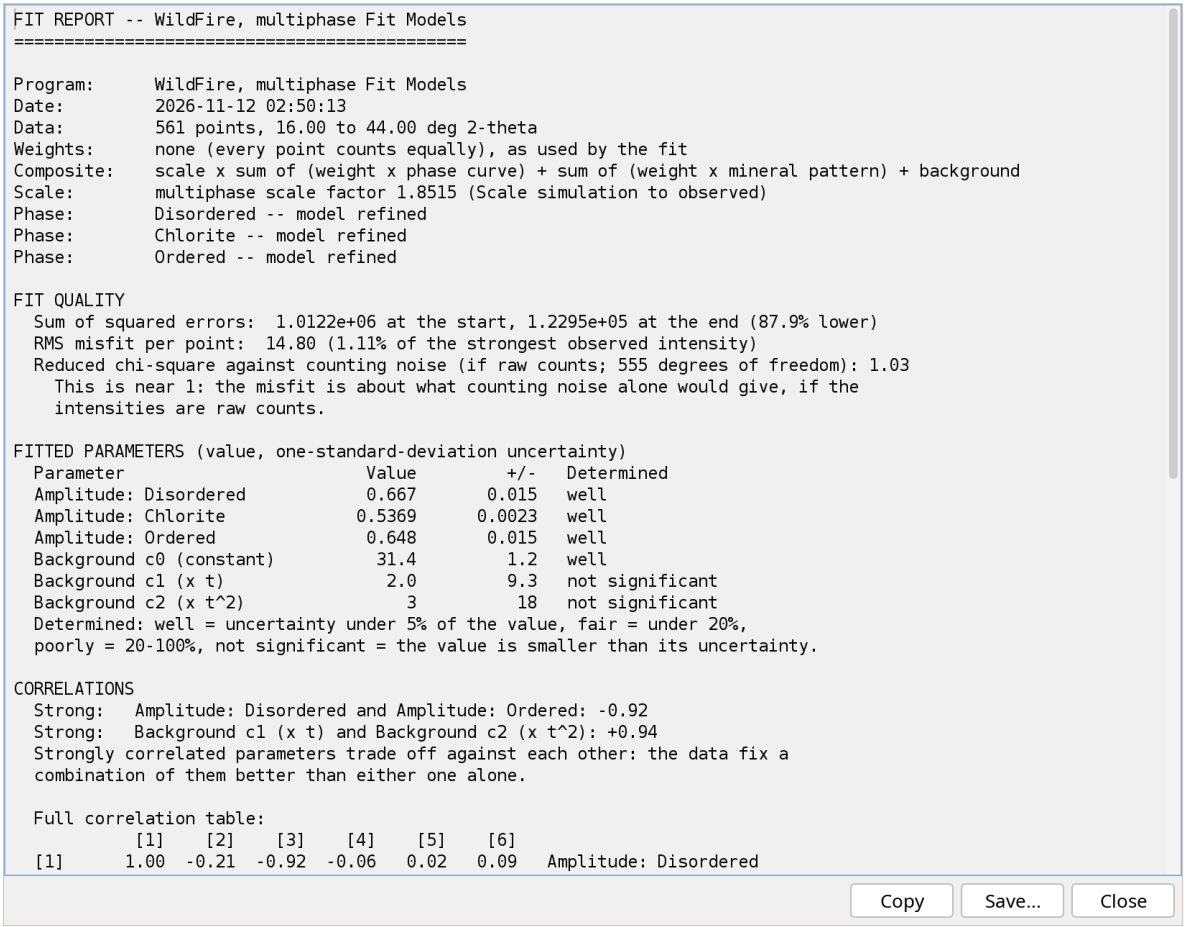


Figure 35. The Fit Report for the Fit Models example above.

Part	What it says
Heading	The fit (Fit Weights or Fit Models), date, the points and 2θ range compared, the weighting (none), how the sum is made, the multiphase scale factor if Scale is ticked, and each phase (model refined or held) and each reference mineral
Fit quality	The sum of squared errors at the start and the end; the RMS misfit per point; and the reduced chi-square against counting noise (section 10)
Fitted parameters	Each phase's weight (its amplitude, weight × scale factor, when Scale is ticked), each mineral's weight and, if fitted, its shift and width, and the three background coefficients, each with its uncertainty and how well it is determined
Correlations	Pairs that trade off against each other, then the full correlation table
Shares	Each phase's and mineral's share of the total integrated intensity, with its uncertainty, and, when Scale is ticked, the phase weights as the proportions on the sliders

Here **Determined** compares each uncertainty with the value itself, since weights have no fixed range: **well** means under 5 % of the value, **fair** under 20 %, **poorly** 20–100 %, and **not significant** means the value is smaller than its uncertainty. The background coefficients are often poorly determined or not significant; that only means the background could be a little flatter or more curved. The report is calculated with the phase patterns held as they are at the end of the fit, so the uncertainties of the weights

do not include those of the phase models; the phases' own parameters are in the single-phase report of a Fit Model on each phase. The background is $c_0 + c_1 t + c_2 t^2$, with $t = (2\theta - 40°) / 40°$.

Tips

- Get each phase close by hand, or with its own Fit Model fit, before fitting the multiphase pattern.
- Tick only the parameters that matter for each phase. Every extra parameter multiplies the number of calculations, and slow structures, such as the Two-Mica (Cis-Trans) options, make each trial slow. Tick **Run in Parallel** on the multiphase view's Fit Settings tab to use all processor cores.
- N1 and N2 change the pattern in small irregular steps rather than smoothly, so a fit can stop at a nearby, slightly wrong value. Fix them at sensible values unless you have a reason to fit them.

Reference minerals (bulk powders)

A bulk-rock or soil sample is mostly quartz, feldspar, carbonate and the like, with the micas, illite and chlorite only a part. Reference minerals add the other minerals to the multiphase pattern: each has a fixed pattern of its own, scaled by a weight, and the phases, the minerals and a smooth background are fitted together. Open the **Minerals** tab in the multiphase view.

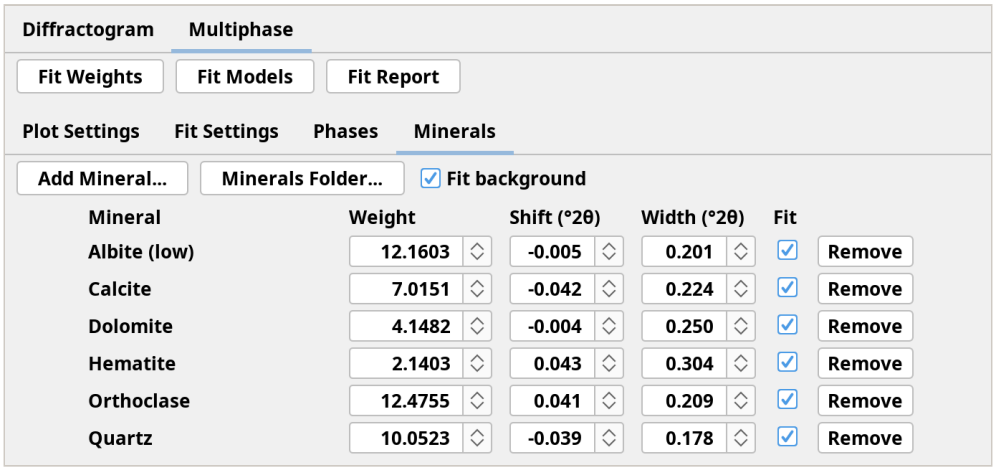


Figure 36. The Minerals tab with six reference minerals after Fit Weights.

Adding minerals. Click **Add Mineral...**, pick one or more from the list (Ctrl-click for several) and click OK. The list shows each mineral's formula and, when one is selected, the crystal structure it was calculated from. A new mineral starts with half the weight that best matches what the multiphase pattern leaves unexplained.

Control	What it does
Mineral	The mineral's name; hold the pointer over it for its formula, source and reference.
Weight	Multiplies the mineral's pattern. 0 leaves the mineral in the list but out of the sum.

Control	What it does
Shift (°2θ)	Moves every peak by this much: sample height, the instrument's zero, or a slightly different composition (Mg in calcite, for example). Typically under ±0.1°.
Width (°2θ)	The peaks' full width at half maximum at 30° 2θ; elsewhere peaks broaden as 1/cos θ, as for small crystallites. Greyed out for a measured pattern, which keeps its own peak shapes.
Fit	Ticked: Fit Weights and Fit Models also fit this mineral's shift and width. A shift may move up to 0.25° per fit, and no further than ±1°, so a peak cannot jump onto a neighbouring one; a width stays within 0.05–0.8°.
Remove	Takes the mineral out of the multiphase pattern.

Fit background, ticked by default, adds a smooth background (a quadratic in 2θ) that Fit Weights and Fit Models fit with the weights and add to the sum. Bulk powders need it even with Remove background ticked, since a little background always remains; without it, minerals tend to widen their peaks to absorb it. Unticking it removes the background from the sum.

Working with a bulk powder

1. Load the pattern and set Low and High 2θ to the range you want fitted.
2. Add the phases as usual, then the reference minerals you can identify. Leave out minerals you are not sure of; Fit Weights sends an absent mineral's weight to 0, so trying one costs little.
3. Click **Fit Weights**. It fits the weights, the background and, for minerals with Fit ticked, the shifts and widths, one mineral at a time, strongest first, over a few passes. Check the difference curve; peaks it leaves unexplained point to minerals not yet included.
4. Then, if you want to refine the phase models, click **Fit Models**.

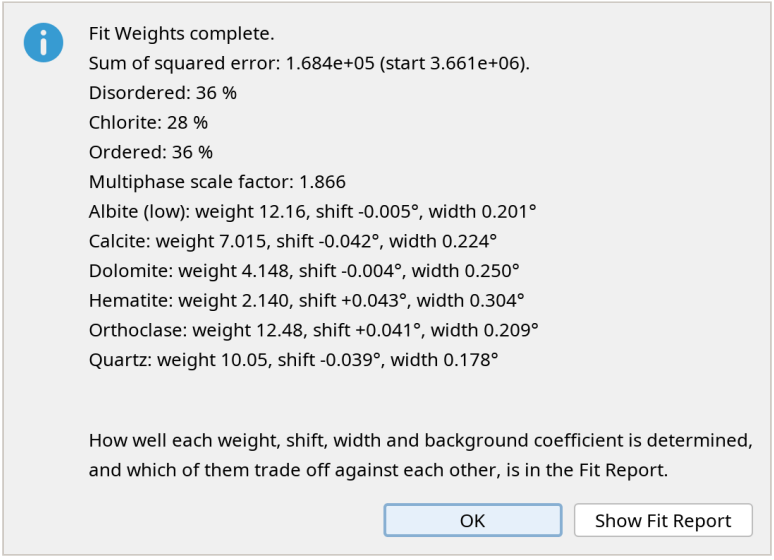


Figure 37. The summary at the end of Fit Weights with six reference minerals.

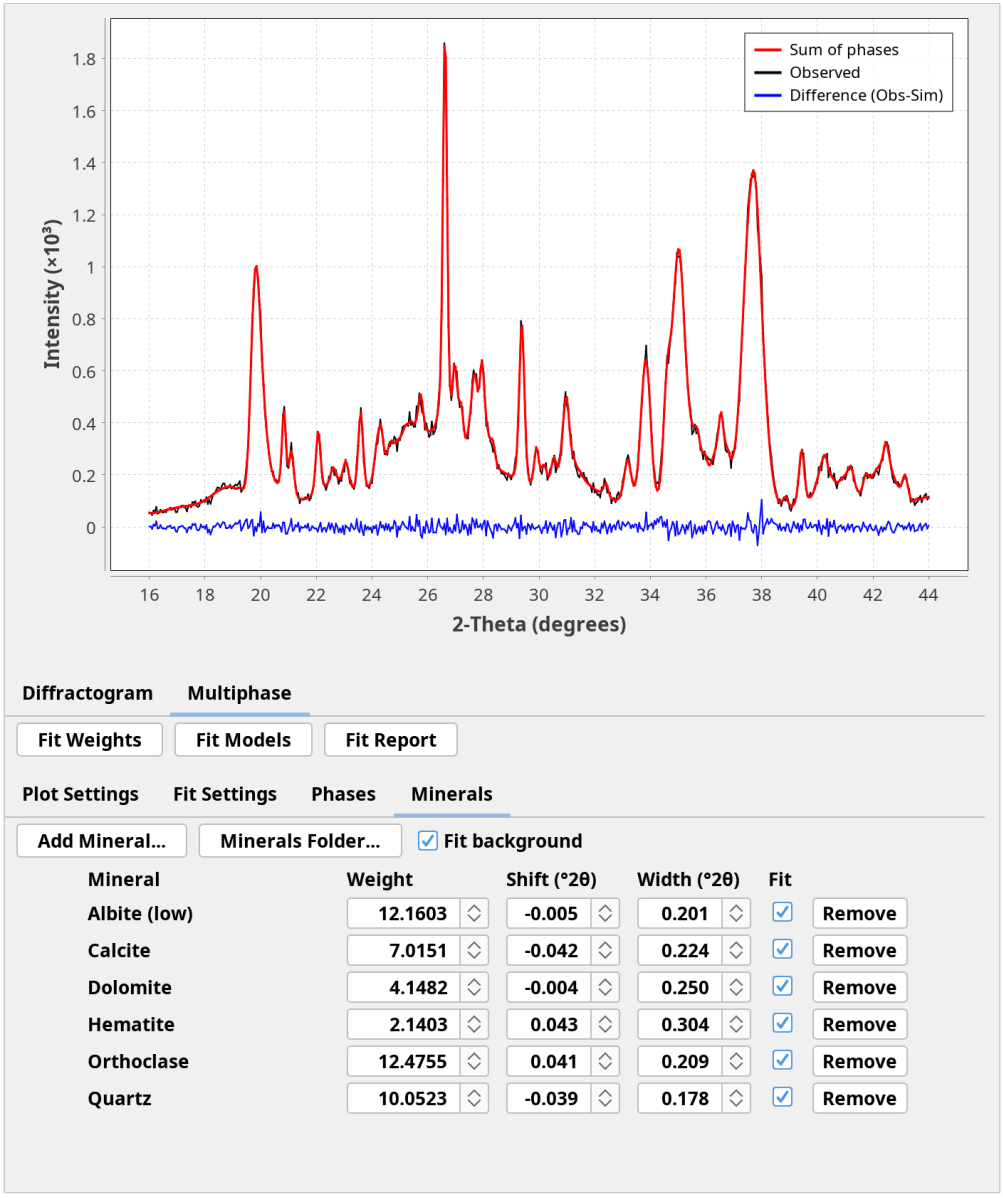


Figure 38. The example pattern of the previous figures with six minerals added, after Fit Weights.

In this example the measured pattern is the one used for Fit Models above, with quartz, low albite, orthoclase, calcite, dolomite and hematite added, each with its own small shift and width. With the six minerals added and Fit ticked for each, one Fit Weights brings the sum onto the measured pattern, with every shift within 0.005° of the value used to make the pattern and every width within 0.015°, except hematite's, the weakest mineral, at 0.30° against 0.28°.

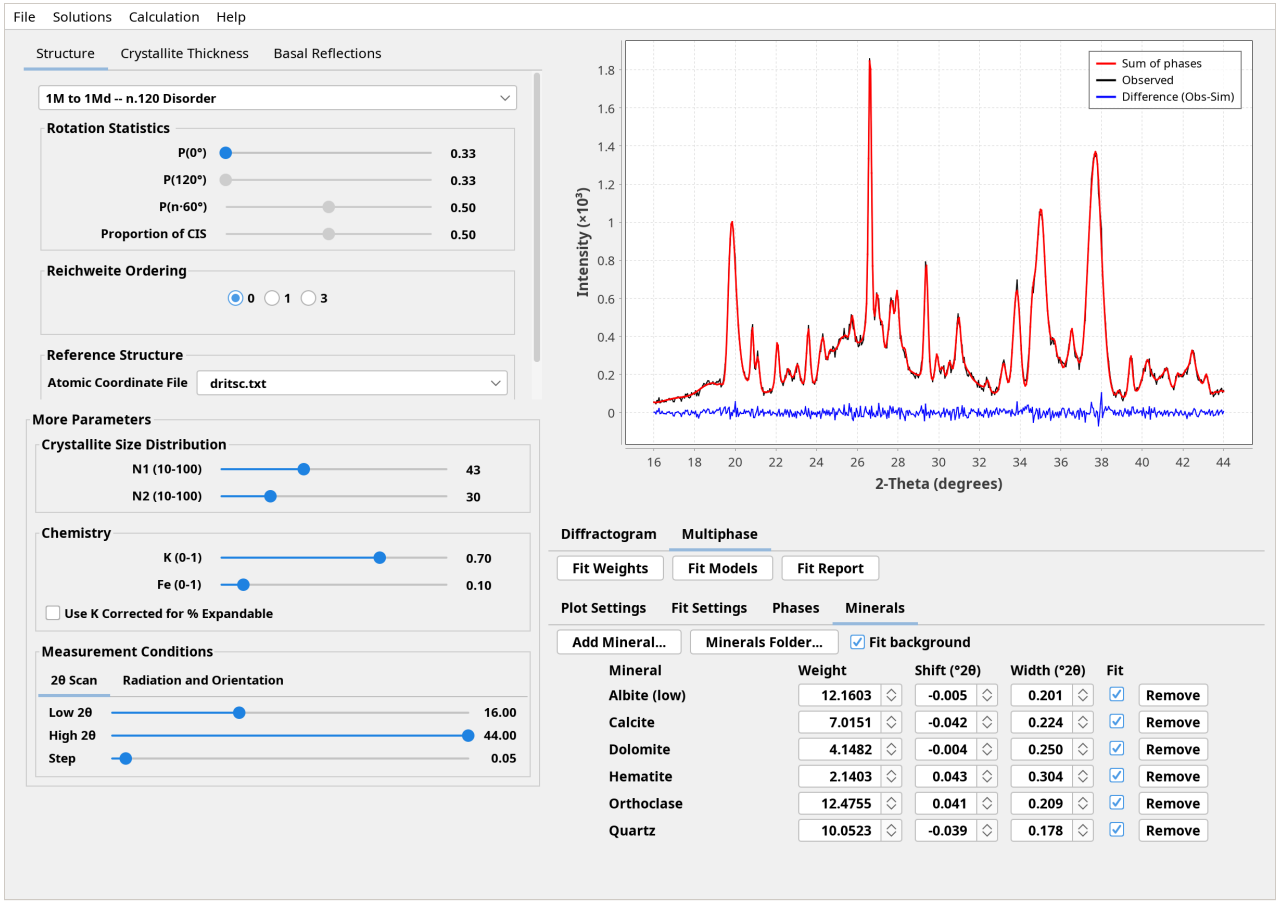


Figure 39. The main window in the multiphase view, with the Minerals tab.

Weights and amounts. The built-in minerals' intensities are per unit mass on one common, calculated scale, so the weights of two built-in minerals are roughly in proportion to their amounts, but not exactly: real intensities also depend on the instrument, the sample's absorption, preferred orientation and particle statistics. For amounts in weight %, mix a known mass of an internal standard (corundum or zincite) into the sample and calibrate each mineral's weight against the standard's with mixtures of known composition.

The built-in minerals

Group	Minerals
Silica	Quartz, Cristobalite
Feldspars	Albite (low), Oligoclase (An28), Andesine (An48), Labradorite (An64), Anorthite, Orthoclase, Microcline, Sanidine
Carbonates	Calcite, Aragonite, Dolomite, Ankerite, Magnesite, Siderite, Rhodochrosite
Fe and Ti oxides	Hematite, Goethite, Lepidocrocite, Magnetite, Ilmenite, Rutile, Anatase
Sulfides, sulfates, halides	Pyrite, Gypsum, Anhydrite, Barite, Jarosite, Halite, Sylvite, Fluorite
Phosphates	Fluorapatite, Hydroxylapatite
Sheet silicates	Talc, Muscovite (2M1)

Group	Minerals
Zeolites	Clinoptilolite-Ca, Analcime
Internal standards	Corundum, Zincite

Each is a list of reflections (d-spacing and intensity) calculated from a published crystal structure in the American Mineralogist Crystal Structure Database (Downs and Hall-Wallace, 2003): for every reflection the structure factor, summed over all symmetry-equivalent reflections, divided by the cell volume squared and by the density. The pattern is drawn when needed, for the wavelength chosen on Radiation and Orientation, with Bragg-Brentano Lorentz-polarization and a pseudo-Voigt peak shape (40 % Lorentzian). The structure used for each mineral is given in the mineral list's description.

Your own minerals. Minerals Folder... opens your own minerals folder, `Minerals` in your WildFire data folder (`C:\Users\<your name>\WildFire\Minerals`), creating it if needed. Every file there appears in Add Mineral's list (marked *your file*), and a file whose mineral name matches a built-in one replaces it. Two kinds of file are read:

- **Patterns**, any text file of 2θ and intensity, one point per line, separated by spaces, tabs, commas or semicolons, in UTF-8 or Windows "Unicode" (UTF-16) text: for example a pattern measured on your own diffractometer, or one exported from another program. The file name is the mineral's name. The pattern is used as it is, so it must be for the same wavelength as your data; only its shift can be fitted.
- **Peak lists**, files ending in `.pks`, in the built-in minerals' format: optional header lines `name:`, `formula:`, `source:` and `reference:`, then one reflection per line, d-spacing in Å and intensity. These work for any wavelength, and their width can be fitted.

Measured patterns of pure minerals from your own instrument, prepared like your samples, give the most reliable weights. A session (section 12) names its reference minerals; one that came from your own minerals folder must still be there when the session is opened, or it is left out with a message.

Saving a multiphase pattern

Choose **File > Save Multiphase Curve...** to write the weighted sum, including any reference minerals and background, to a text file (section 12). To keep the phases themselves, with their models, weights and Refine ticks, and the reference minerals, save a session (**File > Save Session...**, section 12).

12. Files

Saving patterns

File > Save Model Curve... writes the simulated pattern shown on the Diffractogram tab; **File > Save Multiphase Curve...** writes the weighted sum of the phases, with any reference minerals and background. Each opens a save dialog. The file holds one point per line, 2θ and intensity separated by a space, with no header. If you type a name without an extension, `.txt` is added; if the file exists, WildFire asks before overwriting it.

The dialog opens in your Documents folder. The modelFiles and experimentalFiles folders in your WildFire data folder are there if you want one place for your patterns.

A saved pattern is in the same format that File > Input Experimental Curve... reads, so you can load a saved model as the "measured" pattern to compare two models with the difference curve. A pattern file holds no settings; to keep the settings themselves, save the model parameters or a session (below).

Model parameter files

File > Save Model Parameters... saves the model of the solution on screen in one `.wfm` file: every setting of that solution's panel, including its Fit Settings ticks and Run in Parallel, and the measured pattern, if one is loaded. No curve points are written; the settings recreate the pattern exactly. The dialog opens in the modelFiles folder of your WildFire data folder.

File > Open Model Parameters... switches to the file's solution and restores its panel and, if the file holds one, the measured pattern (Low, High and Step then follow it, as on loading a pattern). The other two solutions and the multiphase phases are left as they are, so a saved model can be brought in and added as a phase. Use a model file to keep or exchange one model; use a session to keep everything.

Sessions

A session holds everything needed to carry on where you stopped, in one file:

- the measured pattern itself, so the session does not depend on the original data file;
- every setting of the Disordered, Ordered and Chlorite panels, including the Fit Settings ticks and Run in Parallel;
- the Plot Settings boxes and the solution on screen;
- the phases: each phase's name, solution, model, stored pattern, weight and Refine tick;
- the reference minerals, by name, with their weights, shifts, widths and Fit ticks, and the background.

Choose **File > Save Session...** and give a name; `.wfs` is added. The dialog opens in your WildFire data folder. Choose **File > Open Session...** to reopen one: everything is put back as it was saved and the pattern is recalculated. Opening a session replaces the

current settings, measured pattern and phases, so save first if you want to keep them.

Opening a session file with Open Model Parameters..., or a model file with Open Session..., is refused with a message saying which command to use. None of these commands works while a fit is running.

Model and session files are plain text (Java properties files), so they can be read in a text editor, but edit them only with care.

Atomic coordinate files

Folder	Used by	Coordinates
acfiles	Disordered and Ordered	Orthogonal space
chlorite_acfiles	Chlorite	Orthogonal space
intensities_acfiles	Peak Calculator	Monoclinic space

Each file is plain text. The first line holds a label, *a*, *b*, *c* (Å), β (degrees) and the number of atom lines that follow. Each atom line holds the atom label, the site occupancy and the fractional coordinates *x*, *y* and *z*, separated by commas. Section 4 shows an example. To add a structure, write a file in this form with a text editor, put it in the right folder and restart WildFire; it then appears in the coordinate lists.

For a centrosymmetric cell, list only the top half, *z* from 0 to 0.5, doubling the occupancy of every atom off the $z = 0$ plane (an atom at $z = 0.5$, such as interlayer K, is listed once with its full occupancy). For a cell without a centre of symmetry, list the whole cell and end the file with an atom below the octahedral plane ($z < -0.1$): that is how WildFire recognizes a full cell and adds the sine part of the structure factor (section 4). Chlorite checks the last atom line for this; Ordered checks every line.

Crystallite thickness files

`inputfile\inputfile.txt` (Disordered) and `chlorite_inputfile\chlorite_inputfile.txt` (Chlorite) are read when **Read from INPUTFILE** is chosen. Each holds one number per line:

Line	Holds
1	LOWN, the smallest number of layers in a crystallite
2	N3, the largest number of layers
3 onward	Q(N), the decimal fraction of crystallites that are N layers thick, for N = LOWN to N3, one per line

The Q(N) values should add up to 1. The supplied `inputfile.txt` has LOWN = 1, N3 = 10 and Q(10) = 1, with all other Q(N) zero: an illite made only of crystallites 10 layers thick. That gives illite 00*l* breadths very close to those of the Newmod default distribution of N = 3 to 14. The supplied `chlorite_inputfile.txt` has LOWN = 2, N3 = 6 and Q = 0, 0.735, 0.214, 0.051, 0.01.

Edit these files with any text editor. WildFire reads them at each calculation, so a change takes effect the next time the pattern is recalculated.

13. Support, license and references

Technical support. Report problems and ask questions to R.C. Reynolds III at newmod_for_clays@yahoo.com.

License and disclaimer. WildFire is copyright © 1986–2026 Robert Reynolds. The terms of use, the disclaimer of warranty and the third-party licenses are in `LICENSE.txt` in the installation folder, and under **Help > About WildFire... > Licenses...**.

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