

Newmod III

User Manual

The calculation of one-dimensional X-ray diffraction patterns of mixed-layer clay minerals, and their fitting to measured patterns

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1. About Newmod III

Newmod III computes the 00l X-ray diffraction pattern of a mixed-layer clay from its layer types, their proportions, their ordering (Reichweite) and the instrument settings, and refines those values against a measured pattern.

Mixed-layer clays give broad, overlapping peaks that do not form a rational series, so their patterns cannot be read from lookup tables alone. Newmod III works the other way round: it calculates the pattern of an oriented mount, in which the plate-shaped crystals lie flat on the slide, from a structural model, and the model is changed or fitted until its pattern matches the measured one. The model covers what the basal reflections are sensitive to:

- **Layer proportions and expandability.** The layer types, such as illite and glycolated smectite, and their proportions reproduce the peak migration and intermediate spacings seen between air-dried and glycolated states (sections 5 and 13).
- **Stacking order.** Random (R0) to ordered (R1, R2, R3) interstratification gives the irrational 00*l* series of mixed-layer clays (section 7).
- **Chemistry and crystallite size.** Octahedral iron, interlayer potassium and the distribution of crystallite thicknesses set the peak intensities and breadths (sections 6, 8 and 9), and mixtures of up to four phases can be fitted (section 12).

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 diffraction theory, layer structures and scattering factors are the same as in NEWMODF (R.C. Reynolds, Jr. and R.C. Reynolds III, 1987) and NEWMOD-for-Windows 2 (R.C. Reynolds, Jr. and R.C. Reynolds III). Only the program around them is new.

What is new compared with Newmod 2

Area	Newmod 2	Newmod III
Layer types in one model	2	2 or 3 (tick **Layer 3**)
Ordering	R = 0, 0.5, 1, 1.5, 2, 2.5, 3, or General Case (PB.A, PBA.A, PBAA.A)	R0 to R3, or General Case with one ordering strength per pair of layer types (A-B, A-C, B-C)

Area	Newmod 2	Newmod III
Calculation	Reynolds summation	Reynolds summation or Kakinoki–Komura (transfer-matrix) summation, chosen from the **Calculation > Stacking Method** menu; both give the same pattern
Instrument settings	A Parameters page with Save/Cancel buttons and default columns	Sliders on five tabs that recalculate at once
Fitting	Composition and PA only	Any chosen subset of proportions, ordering, defect distance, sigma-star, mu-star and layer chemistry; a Fit Report gives their uncertainties
Multiphase	Up to 8 phases, weights fitted	Up to 4 phases; weights alone, or each phase's model and weight together; plus 40 non-clay minerals and a background
Background	Not handled	Optional automatic background removal from the observed data
Files	.SXY theoretical and project files	.nm3 model files and .nm3s session files, both with the observed data embedded
Runs on	Windows	Windows installer with its own Java runtime; no separate Java needed

Some Newmod 2 features are not in this version: the black or white plot background, printing, translating the experimental curve, peak integration and labels, and direct editing of d(001). See section 16 for how this affects the old Advanced Techniques.

2. Installing and starting

Newmod III installs from a single Windows installer, `Newmod3C-1.1.0.msi`, and needs nothing else: the Java runtime it uses is included.

1. Double-click `Newmod3C-1.1.0.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\Newmod3C`) and click through to **Finish**.
4. Start the program from the desktop shortcut, or press the Windows key, type `Newmod3C` and press Enter.

What is installed

Item	Location
Program and Java runtime	The installation folder
License for Newmod III	`LICENSE.txt` in the installation folder
Licenses for JFreeChart, Apache Commons Math, FlatLaf, the Noto Sans font and Java	The `licenses` folder, and **Help > About Newmod3C… > Licenses…**
This manual	The `docs` folder, when supplied with the installer

Uninstalling. Open Windows **Settings > Apps > Installed apps**, find Newmod3C and choose **Uninstall**.

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

Decimal separator. Observed data files must use a period as the decimal point, whatever the Windows regional settings (see section 10).

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 three tabs, **Diffractogram**, **Multiphase** and **Treatments**, 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 buttons and its own Plot Settings, Fit Settings and other tabs. The plot keeps the same width and size in both views, so the two can be compared by switching tabs. The pattern is recalculated each time you move a slider or change a selection; there is no Run button for a simple simulation.

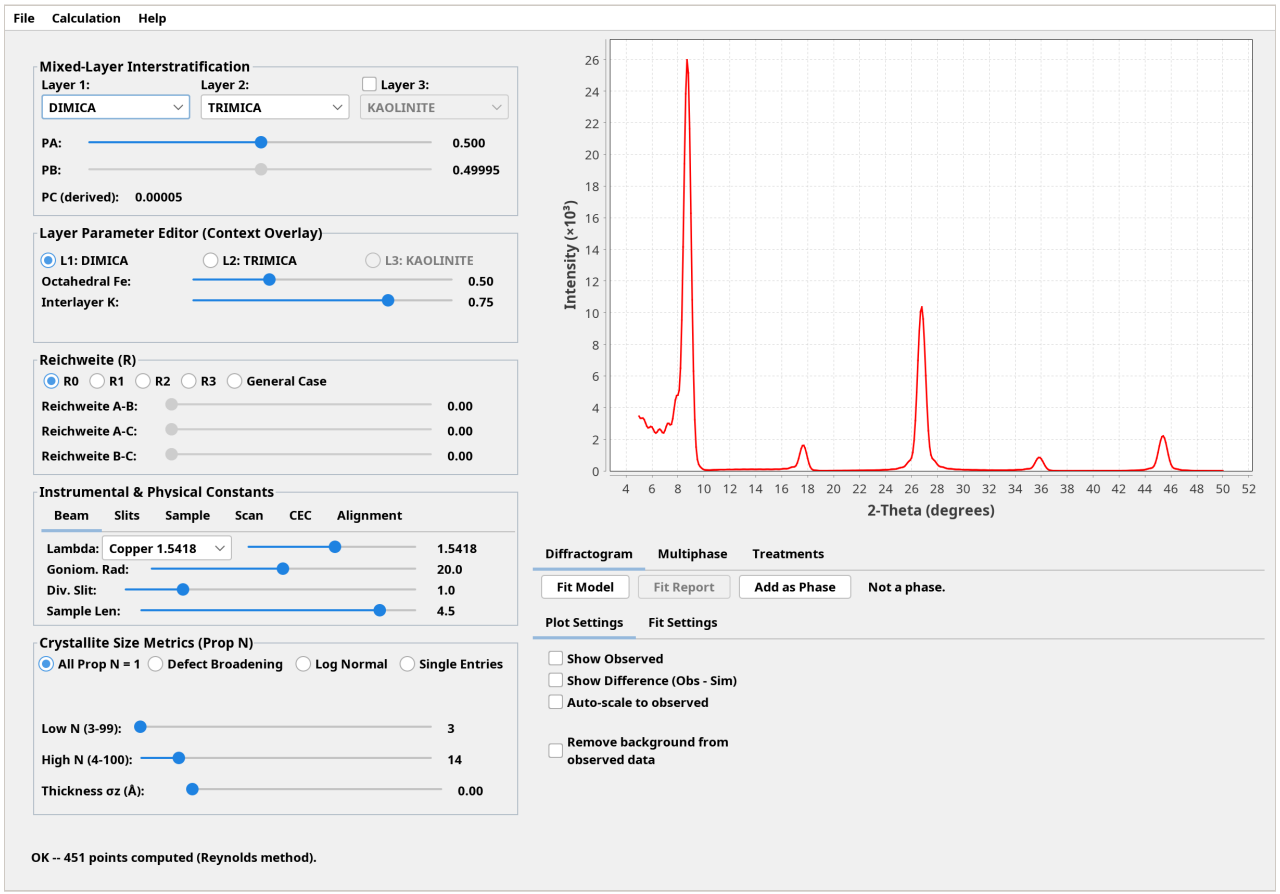


Figure 1. The Newmod III main window, with a two-component DIMICA/TRIMICA model at R0.

Left column, top to bottom

Panel	What it sets	Section
Mixed-Layer Interstratification	The two or three layer types and their proportions PA, PB, PC	5
Layer Parameter Editor	Fe, K and chlorite composition of each layer type	6
Reichweite (R)	The stacking order: R0 to R3 or the General Case	7

Panel	What it sets	Section
Instrumental & Physical Constants	Wavelength, slits, sample, scan range, exchange cation and alignment, on six tabs	8
Crystallite Size Metrics (Prop N)	The distribution of crystallite thicknesses, and the layer-thickness fluctuation σz	9

Right side

Area	What it shows or does	Section
Plot	Single-phase view: the simulated pattern, the observed pattern and their difference. Multiphase view: the weighted sum of up to four phases, any reference minerals and a background, with the observed pattern and the difference	10, 12
Diffractogram tab (below the plot)	Single-phase view. **Fit Model**, **Fit Report** and **Add as Phase**, a line saying whether the model is one of the phases, and the Plot Settings and Fit Settings tabs	10, 11
Multiphase tab (below the plot)	Multiphase view. **Fit Weights**, **Fit Models** and **Fit Report**, and the Plot Settings, Fit Settings, Phases and Minerals tabs	12
Treatments tab (below the plot)	Treatments view: one model fitted to several patterns of the same sample (air-dried, glycolated, heated...). **Fit Treatments**, **Fit Report** and **Check Sensitivity...**, and the Plot Settings, Fit Settings and Treatments tabs	13
Plot Settings tab	Show or hide the observed and difference curves, scale, remove background. The same boxes serve both views	10
Fit Settings tab	Which parameters a fit may change (**Parameters to Fit**; in the multiphase view, each phase's ticks) and how a fit runs (**Optimizer Settings**)	11, 12
Phases tab	The phases: weights, Edit, Update, Cancel and Refine. Multiphase view only	12
Minerals tab	Non-clay reference minerals and the background of the multiphase pattern. Multiphase view only	12

If a calculation fails, for example because the ordering cannot exist at the chosen proportions, the status line shows **Calculation error** in red and the plot keeps the last good pattern.

4. File, Calculation and Help menus

The File menu reads observed data and saves or restores your work; the Calculation menu chooses how one step of the calculation is carried out; the Help menu shows the version, copyright and licenses.

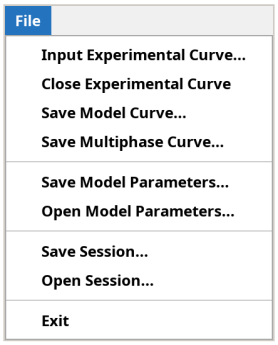


Figure 2. The File menu.

Command	What it does	File type
Input Experimental Curve...	Loads a measured pattern to compare and fit against (section 10)	Text, two columns
Close Experimental Curve	Unloads the measured pattern: the plots drop it, Show Observed and Show Difference are turned off, and the scan range is free again (section 10)	
Save Model Curve...	Saves the curve on the Diffractogram plot as 2-theta and intensity, separated by a space	`.txt`
Save Multiphase Curve...	Saves the multiphase pattern (the weighted sum of the phases, reference minerals and background) the same way	`.txt`
Save Model Parameters...	Saves the displayed model as its settings, not its curve points, plus the observed data if loaded	`.nm3`
Open Model Parameters...	Restores a `.nm3` model and its observed data and recalculates; replaces the displayed model	`.nm3`
Save Session...	Saves everything: the displayed model, the observed data, all four phases with their weights, and the reference minerals and background	`.nm3s`
Open Session...	Restores a session; replaces the displayed model, the observed data, all four phase slots and the reference minerals	`.nm3s`
Exit	Closes the program; unsaved work is lost	

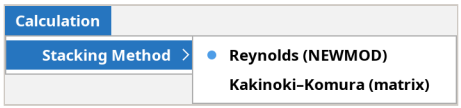
Help command	What it does
About Newmod3C...	Version, copyright and third-party credits; **Licenses...** shows each license in full

Model and session files. A saved model or session holds the settings that produce the curve, not the curve itself, so it stays small and reproduces the pattern exactly when opened. The observed data is copied into the file, so the file still works after the original data file is moved or deleted. A session names its reference minerals; one that came from your own minerals folder must still be there when the session is opened. The files are plain text and can be read in any text editor, but edit them by hand only with care.

Curve files. The `.txt` files hold one point per line, 2-theta then intensity, for use in spreadsheets and plotting programs. The 2-theta values are rounded so the step is exact; intensities keep full precision.

Saving, opening and closing the experimental curve are blocked while a fit is running; wait for it to finish or cancel it first.

Calculation menu



The Calculation menu, with Stacking Method open.

Stacking Method chooses how Newmod III adds up the contributions of every possible sequence of layers in a crystallite, for every pattern it calculates: the Diffractogram plot and every pattern of Fit Model and Fit Models. Both choices give the same pattern; only the method and the speed differ (section 15).

Choice	How the sum is calculated
Reynolds (NEWMOD)	The layer compositions of all domains are tabulated (Bethke and Reynolds, 1986) and their phases summed, as in NEWMOD (Reynolds, 1980). The default.
Kakinoki–Komura (matrix)	The same sum as a product of transition matrices (Kakinoki and Komura, 1952; Drits and Tchoubar, 1990). Much faster with three layer types, a large High N, or R2 and R3, which shortens fits considerably.

What the choice does not change. Both use Reynolds' model throughout: the layer structures and scattering factors, the ordering (Reichweite) parameters, the crystallite thickness distribution, the Lorentz-polarization and orientation corrections, and the intensity formula. Only the summation differs, and because both methods are exact they agree to rounding error. Choosing Kakinoki–Komura therefore does not make Newmod III equivalent to programs built on the complete approach of Drits and co-workers, such as Sybilla, which make different physical choices (interlayer structures, scattering factors, orientation corrections) and can give different patterns for the same nominal inputs. The agreement of the two methods shows that the sum is calculated correctly; it is not a comparison of Reynolds' model with Drits'.

The status line under the left column names the method that produced the curve on screen, for example **OK -- 451 points computed (Kakinoki–Komura method)**. The choice is remembered the next time the program starts. It cannot be changed while a fit is running: a fit uses the method that was selected when it started.

5. Layer types and proportions

Choose each layer type from its drop-down list, then set how much of each the crystallites contain: PA for Layer 1 (component A), PB for Layer 2 (B) and PC for Layer 3 (C), always summing to 1.

Each list offers 20 layer types (section 16): Layer 1 starts as DIMICA, Layer 2 as TRIMICA and Layer 3 as KAOLINITE. Newmod III adds two more, DISMECTITE-HEATED and TRISMECTITE-HEATED, for smectite collapsed by heating.

Two-component mode (Layer 3 unticked, the default)

- Layer 3 is greyed out and contributes nothing: PC is held at 0.00005, small enough to have no visible effect.
- PA is the more abundant layer type, as in Newmod 2, so its slider stops at 0.500 and runs to 0.990.
- PB follows automatically as 1 − PA − 0.00005; its slider moves on its own.

Three-component mode (Layer 3 ticked)

- PA and PB each run from 0.005 to 0.990 and PC (derived) shows the remainder.
- PA + PB cannot exceed 0.995, so PC is never less than 0.005. If moving one slider would break that limit, the other slider gives way.
- Any of the three may be the most abundant.

Layers of the same mineral. Two or three layers set to the same mineral are one layer type, so they share one set of chemistry (Fe, K and the chlorite values, section 6). Editing either layer in the Layer Parameter Editor changes both, and a layer switched to a mineral that another layer already holds takes the values that layer has. A note beside PC names the linked layers, for example *L1 = L2: same chemistry*. (Two layers of one mineral with different chemistry would be two different minerals interstratified, not one.)

Pure minerals. As in Newmod 2, a single mineral is modelled by setting Layer 1 and Layer 2 to the same type (and Layer 3 too, if it is ticked). The layers are then identical, so the proportions and the Reichweite have no effect on the pattern: PA, PB, the Reichweite choices and the General Case sliders are greyed out, a note beside PC reads *Pure mineral*, and a fit never refines them. With two of three layers the same, only their chemistry is linked; the proportions stay active.

The program remembers the Fe, K and chlorite values you set for each mineral in each layer. If you switch a layer to another mineral and back, its earlier values return, unless the layer is linked to another layer of that mineral, whose values it then takes.

Separate phases of a multiphase pattern (section 12) are separate models, so two pure DIMICA phases, for example, can have different chemistry. A model or session saved before this rule, with two layers of one mineral at different chemistry, opens with the later layer taking the earlier layer's values.

6. Layer Parameter Editor

This panel sets the chemistry of one layer type at a time: pick **L1**, **L2** or **L3** at the top, and the sliders below change to the ones that layer's mineral uses. Layers of the same mineral share their values (section 5), so picking either shows, and changes, the same values.

Mineral selected	Sliders shown	Range
DIMICA	Octahedral Fe; Interlayer K	0–1.70; 0–1.00
TRIMICA	Octahedral Fe; Interlayer K	0–3.00; 0–1.00
DISMECTITE (all forms), DIVERMICULITE	Octahedral Fe	0–1.70
TRISMECTITE (all forms), TRIVERMICULITE, SERPENTINE	Octahedral Fe	0–3.00
DI-DICHLORITE	Chlorite Silicate Fe; Chlorite Hydrox Fe; Hydroxide Layer	0–2.00; 0–2.00; 0–1.00
TRI-TRICHLORITE	the same three	0–3.00; 0–3.00; 0–1.00
DI-TRICHLORITE	the same three	0–2.00; 0–3.00; 0–1.00
TRI-DICHLORITE	the same three	0–3.00; 0–2.00; 0–1.00
KAOLINITE	none (fixed composition)	

What the values mean (unchanged from Newmod 2)

- **Octahedral Fe** is the number of Fe atoms in the octahedral sheet per Si_4O_{10} (per Si_2O_5 for serpentine). Fe replaces Al in dioctahedral layers, which is why the maximum is 1.70, and Mg in trioctahedral layers, where the maximum is 3.00.
- **Interlayer K** is the number of K atoms per Si_4O_{10} in a mica layer. For illite, a typical value is 0.7.
- **Chlorite Silicate Fe** is Fe per three octahedral sites in the 2:1 layer; **Chlorite Hydrox Fe** is Fe per three sites in the hydroxide interlayer.
- **Hydroxide Layer** is how complete the hydroxide interlayer is. 1 is a normal chlorite; as the value falls toward 0, the structure and its pattern approach those of vermiculite.

A chlorite's name gives its two sheets in order: silicate layer, then hydroxide layer. DI-TRICHLORITE, for example, has a dioctahedral 2:1 layer and a trioctahedral hydroxide sheet. That is why its two Fe sliders have different maximums.

The radio buttons show each layer's mineral name; hover over one to see the full name if it is cut off.

7. Reichweite (stacking order)

The Reichweite (R) sets how far back in the stack a layer "looks" when deciding what type it is: R0 is random interstratification, and R1, R2 and R3 are increasingly long-range ordering.

R0 to R3. Choose one and the program works out the ordering itself: it pushes the ordering at that level, and every level below it, as far as the current proportions allow. For two components this matches Newmod 2's discrete choices R = 0, 1, 2 and 3. No probabilities need to be entered.

General Case. Choose General Case to set the ordering yourself with three sliders, which are greyed out for R0 to R3:

Slider	Controls
Reichweite A-B	Ordering between Layer 1 and Layer 2
Reichweite A-C	Ordering between Layer 1 and Layer 3
Reichweite B-C	Ordering between Layer 2 and Layer 3

Each runs from 0.00 to 1.00. At 0 the two layer types follow each other at random. Toward 1 they increasingly alternate, so a layer of one type is ever more likely to be followed by the other, up to the maximum the proportions allow. In two-component mode only A-B has any effect.

The General Case is R1 ordering with an adjustable strength. For two components, A-B = 0.50 gives Newmod 2's R = 0.5, and A-B = 1.00 gives R = 1. Newmod 2's R = 1.5 and 2.5, and its direct entry of PBA.A and PBAA.A, have no equivalent in this version.

Nonsense Ordering. If the three sliders together ask for more alternation than the proportions allow (one layer type would have to be followed by the others more often than it occurs), the red label **Nonsense Ordering** appears beside General Case and the pattern is not recalculated. Lower one of the sliders until the label disappears.

Limits to know about

- In two-component mode, R3 can give the same pattern as R2, because R2 already uses up the ordering the proportions allow.
- Fitting (section 11) refines only R1-type ordering. Pressing **Fit Model** with R0 to R3 selected switches the panel to General Case first, keeping the same ordering: R0 and R1 are General Case settings already (all strengths 0, or each at its maximum), so the pattern does not change. R2 and R3 have no General Case equivalent and start from the R1 ordering.

8. Instrumental and physical constants

These six tabs describe your diffractometer, sample and scan. They replace Newmod 2's Parameters page; the defaults are the same, so for most work you need not change them.

Beam

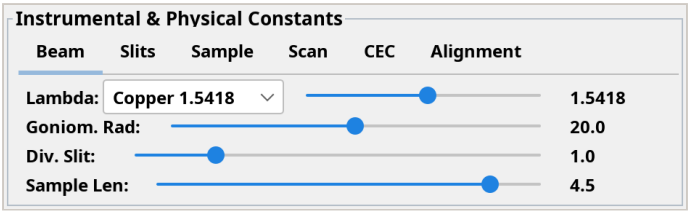


Figure 3. The Beam tab.

Setting	Default	Range	Meaning
Lambda	Copper 1.5418	0.5000–2.5000 Å	Wavelength of the incident radiation. The list offers Copper 1.5418 and Cobalt 1.7902; moving the slider to any other value shows Custom.
Goniom. Rad	20 cm	15–25 cm	Goniometer radius
Div. Slit	1.0°	0.01–5.00°	Divergence of the primary beam. With the radius and sample length it corrects the intensity lost at low angles when the beam footprint is longer than the sample.
Sample Len	4.5 cm	1.25–5.0 cm	Length of the sample along the beam

Absolute intensities are realistic only for CuKα, because the empirical calibration constants were measured only for that radiation. Intensity ratios between minerals are correct at any wavelength.

Slits

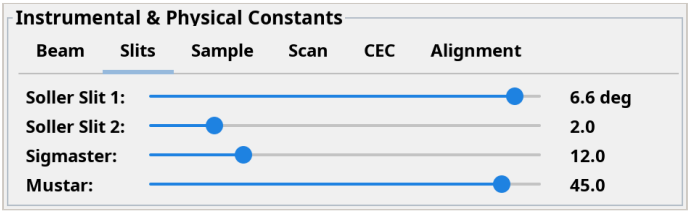


Figure 4. The Slits tab.

Setting	Default	Range	Meaning
Soller Slit 1	6.6°	1.0–7.0°	Primary (incident-beam) Soller slit. 6.6° is the Siemens D-500 value and suits instruments with no primary Soller slit.
Soller Slit 2	2.0°	1.0–7.0°	Diffracted-beam Soller slit

Setting	Default	Range	Meaning
Sigmaster (σ*)	12	0–50°	Standard deviation of the crystallite orientation about the sample plane. With the Soller slits it controls the Lorentz factor, and so absolute intensity and its change with angle.
Mustar (μ*)	45	0–50	Mean mass absorption coefficient of the sample. 45 is a nominal value for low-Fe clays with CuKα. It affects absolute intensity only.

Sample

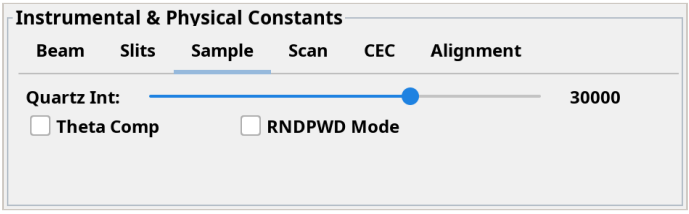


Figure 5. The Sample tab.

Setting	Default	Range	Meaning
Quartz Int	30000	10000–40000	Counts per second at the top of the 3.34 Å (101) peak of randomly oriented quartz, measured on your instrument with the same slits and radius. Puts the calculated intensities on an absolute basis.
Theta Comp	unticked		Ticked: a theta-compensating (variable) divergence slit, which keeps the irradiated length constant; intensities are multiplied by sin θ. Unticked: a fixed divergence slit; at low angles, where the beam is longer than the sample, intensity is reduced by sample length ÷ beam footprint.
RNDPWD Mode	unticked		Ticked: the random-powder Lorentz-polarization factor, $(1 + \cos^2 2\theta) / \sin^2 \theta$; σ* and the Soller slits then have no effect. Unticked: the oriented-aggregate factor, $\psi (1 + \cos^2 2\theta) / \sin \theta$, with ψ from σ* and the Soller slits.

Note on the two check boxes. The defaults (both unticked) match Newmod 2's defaults: slit out, RNDPWD no. Neither box is a simple scale factor: each changes how intensity varies with angle, so use the same settings for every phase of a multiphase pattern. Model and session files saved by earlier versions, in which these boxes had the opposite meaning, open with the boxes reversed; set them again after opening such a file.

The random-powder Lorentz factor is the right choice for standardizing randomly oriented powders. It gives correct peak intensity ratios but not correct absolute intensities. With a theta-compensating slit, all intensities are multiplied by sin θ and normalized to the standard geometry at 26.65° 2θ.

Scan

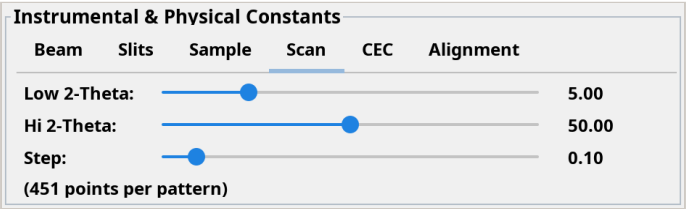


Figure 6. The Scan tab.

Setting	Default	Range
Low 2-Theta	5.00°	2.00–15.00°
Hi 2-Theta	50.00°	20.00–80.00°
Step	0.10°	0.01–1.00°

The line below shows how many points each pattern has. A coarse step can miss the true top of a narrow peak; finer steps take longer, which matters most when fitting. The scan range is shared by all phases. When observed data is loaded, Low and Hi are limited to the observed range, and they set the window a fit uses (section 11).

CEC

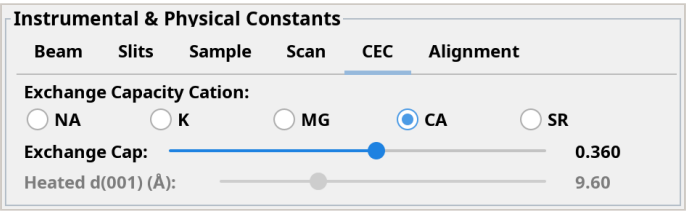


Figure 7. The CEC tab.

Setting	Default	Range	Meaning
Exchange Capacity Cation	CA	NA, K, MG, CA, SR	The exchangeable cation in smectite interlayers
Exchange Cap	0.360	0.250–0.450	Univalent exchangeable cations per 4(Si, Al). For Ca, Mg and Sr the number of cations is half this value.
Heated d(001) (new)	9.60 Å (dioctahedral), 9.70 Å (trioctahedral)	9.30–10.30 Å	Basal spacing of the heated, collapsed smectite layer types (section 16). Greyed out unless one is in use. Choosing a heated layer type sets its default.

The cation settings apply only to smectites, and Heated d(001) only to the heated smectite types. The cation in one-layer glycol smectite is always Na, because apparently only that cation forms the one-layer glycol complex.

Alignment (new in Newmod III)

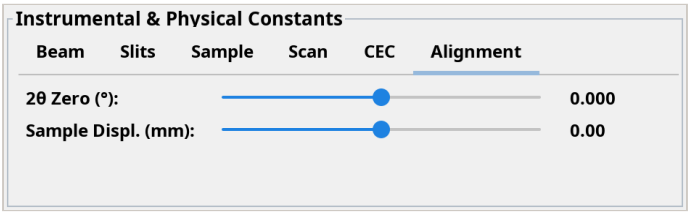


Figure 8. The Alignment tab.

Setting	Default	Range	Meaning
2θ Zero (°)	0.000	−0.500 to +0.500	The instrument's zero error. Every calculated peak moves by this amount; positive moves peaks to higher angles.
Sample Displ. (mm)	0.00	−1.00 to +1.00	How far the sample surface lies above (+) or below (−) the goniometer axis. A sample that is too high moves peaks to higher angles, one that is too low to lower angles, by an amount that falls slowly with angle (section 15).

Both move the calculated pattern sideways to match how the measured one was recorded; neither changes peak heights or shapes. They matter most for the low-angle basal peaks of expandable clays, where a small error in 2θ is a large error in d-spacing. Uncorrected, a shift is easily mistaken for mineralogy: in a test, a DIMICA/TRIMICA pattern calculated with PA = 0.70 and a sample 0.35 mm too high was fitted at PA = 0.90 with no displacement allowed for, and at 0.70 with Sample Displ. refined. A zero error of 0.08° did the same on a smaller scale, giving PA = 0.78.

If you know the sample height or the zero error, for example from an internal standard such as quartz, enter it here. Otherwise both can be refined (section 11). The two are hard to tell apart over a narrow range of angles, since both move every peak by nearly the same amount there; refine one of them unless the pattern covers a wide range. Leave both at 0 for data the instrument software has already corrected.

9. Crystallite size (Prop N)

N is the number of unit cells stacked in a coherently scattering crystallite, and Prop N is how much of the sample has each thickness. Choose one of four distributions. **High N** (default 14, range 4–100) bounds all of them, and **Low N** (default 3, range 3–99) the first and last. High N is always at least one more than Low N; moving one slider past the other pushes it along.

All Prop N = 1 (the default). Every thickness from Low N to High N is equally abundant. With the defaults the sample holds equal volumes of crystallites 3, 4, 5 ... 14 layers thick. Peaks have a broadly Gaussian shape.

Defect Broadening. Models line broadening from randomly spaced stacking faults along Z (Ergun, 1970), and gives very realistic peak shapes, particularly for pure minerals. Low N is fixed at 1 while this is selected, and the slider **Mean Defect Free Dist** (δ, default 38.60, range 1.00–100.00) appears. δ is the average number of unit cells between faults, and the proportion of each thickness falls off exponentially, $P(N) = \exp(-N/\delta)$. This differs from Newmod 2's exp(−(N−1)/δ) only by a constant factor, which disappears because P(N) is normalized to a sum of 1. Realistic δ for clays is 3 to 10. For ideal defect broadening, set High N to 7δ; below that, finite crystallite size starts to show and peaks become more Gaussian. The authors' experience is that High N = 5δ is the most realistic choice for clay minerals. High N can now go to 100 (50 in Newmod 2).

Log Normal. 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. Low N is fixed at 1, and two sliders appear: **Mean N** (default 10.0, range 1.0–100.0) and **Width β^2** (default 0.30, range 0.01–1.50), the variance of ln N. Then

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

where $\bar{N}$ is Mean N. The distribution peaks at $\bar{N}e^{-3\beta^2/2}$, not at one layer as defect broadening does. High N cuts it off, so set High N well above Mean N: with Mean N = 30, β^2 = 0.30 and High N = 100 the mean actually used is 29.4.

Single Entries. Enter your own distribution one thickness at a time. Two controls appear: choose a thickness N with Entry Index (limited to Low N–High N), then set its relative abundance with the value slider (1–100; every thickness starts at 50). Only the relative values matter, since the distribution is normalized. Each change recalculates the pattern, so there is no Apply button.

Thickness σz (Å) (new in Newmod III; default 0.00, range 0.00–1.00, under all four options). Real layer spacings are not all identical: water content, cations and layer chemistry make each spacing vary a little about its mean d(001). σz is the standard deviation of that variation, each spacing varying independently of its neighbours (Drits

and Tchoubar, 1990; Ferrage et al., 2005). The variations add up over the height of a crystallite, so they broaden and weaken the peaks more and more with angle: with a pure DIMICA model and σz = 0.2 Å, the 001 peak is almost unchanged while the 005 peak is more than twice as wide. Crystallite thickness broadens all orders more evenly, so the way peak width grows with angle is what tells the two apart. At 0 the calculation is exactly that of NEWMOD. The equation is in section 15.

A fit uses whichever of these options is selected and leaves it selected. Mean Defect Free Dist is refined only when Defect Broadening is selected, and Mean N and β^2 (listed as Mean N (log-normal) and β^2 (log-normal)) only when Log Normal is selected. σz (listed as σz (layer thickness)) can be refined under any option, but is unticked by default (section 11).

10. Plots, observed data and Plot Settings

The Diffractogram tab plots the simulated pattern in red, the observed pattern in black and their difference (observed minus simulated) in blue.

Reading the plot

- Move the pointer over the plot to see its 2θ and the matching d-spacing (Bragg's law with n = 1 and the current Lambda) in a box under the legend.
- Drag a rectangle from left to right to zoom in. Drag from right to left to return to the full view.
- Right-click the plot for the chart's own menu, which includes copying, saving and printing the plot as an image.

Loading observed data. Choose **File > Input Experimental Curve...** and pick a text file with one point per line: 2θ, then intensity, separated by spaces, tabs or a comma. Lines that are not two numbers, such as headers, are skipped. The decimal point must be a period. The points need not be evenly spaced or in order.

After loading, the observed curve is shown, and **Low**, **Hi 2-Theta** and **Step** on the Scan tab are set to match the observed data (Step to the nearest value the slider can show, below). They are not locked: you can still move them anywhere, for example to calculate beyond the measured range. **File > Close Experimental Curve** unloads the data when you no longer need it. There is no need to match Newmod 2's fixed step sizes.

Steps the Step slider cannot show. Step moves in hundredths of a degree. When the observed data's step is not a whole number of hundredths (0.0167° or 0.005°, for example), Newmod III linearly interpolates the observed data onto the scan points, Low 2-Theta plus whole multiples of Step, so that every observed point used falls on a calculated one, and the status line says so. This is done again whenever Low or Step changes. The observed curve, the difference curve, Auto-scale, background removal and every fit then use the interpolated points. With a Step coarser than the data's own step, the interpolation reads the observed 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 data's own to use all of it. Model and session files keep the observed data as loaded.

Plot Settings tab



Figure 9. The Plot Settings tab.

Control	What it does
Show Observed	Shows or hides the observed curve. Turning it off also turns off the difference curve.
Show Difference (Obs - Sim)	Shows the observed minus simulated curve. Turning it on also shows the observed curve.
Auto-scale to observed	Rescales the height of the simulated curve, not its shape, to best match the observed data, and shows the factor used. Display only: no model value changes, and phases are stored without it. Useful while you adjust sliders by hand, since proportion, ordering and broadening changes can move the raw intensity a great deal.
Remove background from observed data	Subtracts a slowly varying background (air scatter, sample holder, amorphous material) from the observed data, estimated automatically by the SNIP algorithm. Newmod III calculates only the scattering from the layer stack, so an uncorrected background is a mismatch that has nothing to do with the mineralogy. This changes the observed and difference curves, auto-scaling and what a fit is fitted against. Off by default.

The first three need observed data; without it the program asks you to load a file first.

11. Fitting one model

In the single-phase view (the **Diffractogram** tab below the plot), **Fit Model** adjusts the parameters ticked on the **Fit Settings** tab until the pattern of the model in the panel best matches the observed pattern, starting from the values currently on screen.



Figure 10. The Fit Settings tab in two-component mode, with Fit Model above it: Parameters to Fit on the left, with Check Sensitivity... below the ticks, and Optimizer Settings on the right.

Which model is in the panel. A line beside the buttons says whether the model in the panel is one of the phases (section 12):

- **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 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.

Before you fit

1. Load the observed pattern (**File > Input Experimental Curve...**) and decide whether to tick **Remove background from observed data** (section 10).
2. Set **Low 2-Theta** and **Hi 2-Theta** on the Scan tab to the range you want fitted. Only that window is used.
3. Choose the layer types by hand and bring the model reasonably close: rough proportions, an ordering, sensible chemistry. The fit refines from where you start and finds the nearest good match, not necessarily the best one overall. Auto-scale to observed helps you judge the shape while you do this.
4. On **Fit Settings**, under **Parameters to Fit**, tick the parameters to refine; unticked ones stay at their current values.

What can be refined

The list depends on the layer types chosen; scroll it if needed.

Parameter	Fitted range	Notes
PA	0.50–0.99 (two components); 0.02–0.96 (three)	
PB	0.02–0.96	Three-component mode only
Reichweite A-B	0–1	
Reichweite A-C, B-C	0–1	Three-component mode only
Defect Distance	1–100	Refined only with Defect Broadening selected; otherwise left unchanged
Sigma*	1–50	
Mu*	not refined	Mu* only scales the whole pattern, which every fit already does exactly, so its box is greyed out
σz (layer thickness)	0–1.00 Å	Unticked by default. It widens peaks more and more with angle, so it trades against the crystallite-size parameters; refine it deliberately, ideally once the crystallite size is roughly right (section 9)
2θ zero shift	−0.50 to +0.50°	Unticked by default (section 8). Held in multiphase fits
Sample displacement	−1.00 to +1.00 mm	Unticked by default (section 8). Over a narrow range of angles it trades almost exactly against the zero shift, so refine one of the two. Held in multiphase fits
Heated spacing (Å) (new)	9.30–10.30 Å	Shown only when a heated smectite layer is in use, on the panel or in a pattern of the Treatments view. Unticked by default. With illite it trades against the proportions (section 16), so fit it from a pattern with several orders
Fe (Layer n)	0 to 1.70 or 3.00	Layers that have octahedral Fe
K (Layer n)	0–1	Mica layers only
Sil Fe, Hyd Fe, Hyd Layer (Layer n)	as in section 6	Chlorite layers only

Layers of the same mineral have one set of chemistry parameters, listed under the first of them: two DIMICA layers give one **Fe (Layer 1)** and one **K (Layer 1)**, applied to both. For a pure mineral the PA, PB and Reichweite boxes are greyed out and never refined, since they have no effect (section 5).

Ordering is always fitted as General Case (R1) strengths; R2 and R3 cannot be refined.

Fit settings

The **Optimizer Settings** box on the right of Fit Settings holds settings shared by **Fit Model** and **Fit Models**. **Fit Weights** solves for the weights directly and does not use them.

Control	Default	What it does
Peak-only rough fit for large datasets	ticked	First fits only the automatically detected peak regions, which is fast, then polishes against the full window. This is what lets a large dataset (around 2,500 points) converge in reasonable time; for smaller ones it makes little difference.
Peak fit timeout (min)	2	Time limit for the peak-only stage (1–60). Greyed out when the rough fit is unticked.
Full-range timeout (min)	6	Time limit for the full-window stage (1–60). Raise it for large datasets.
Run in parallel	ticked	Uses all processor cores. Untick only if you need the computer for something else during a fit.

Running a fit

1. Click **Fit Model**. If R0 to R3 is selected, the Reichweite panel switches to General Case first (section 7). The fit starts from exactly the pattern on screen.
2. The button changes to **Cancel** and the plot updates as the fit improves. Click **Cancel** to stop; the latest result is kept.
3. When the fit ends, the uncertainties are estimated for the Fit Report (a few seconds; the status line says so), and then a summary lists each refined value before and after, the overall scale factor and the improvement in fit. If a stage timed out or failed, a warning at the top of the summary says so: the values shown are then the starting point of that stage, not a fitted result. **Show Fit Report** in the summary opens the Fit Report (below).
4. The panel is set to the fitted values, with General Case selected. The crystallite-size option is not changed.

How the match is measured. The fit minimizes the weighted squared difference between observed and simulated intensities, with each point weighted by 1 / intensity, so weak features count as well as strong peaks. It runs in two passes: the first weights each point by its observed counts; the second, starting from the first result, weights it by the fitted pattern instead. Counting noise depends on the true intensity, which the fitted pattern estimates without the noise. Weights from the observed counts give too much weight to points where the noise happened to fall low, and in tests this pulled parameters that change the relative intensities, such as K and Sigma*, off by about one standard deviation; the second pass removes that bias. The second pass starts close to the answer, so it usually takes a fraction of the first one's time. The overall intensity scale is calculated exactly at every step rather than fitted, so a difference in absolute intensity cannot distort the mineralogical parameters.

When a fit goes out of date. If you later change the 2θ window, the model, the observed data or the background setting, a red notice in the corner of the plot says the fit result no longer matches what is on screen, and why. It disappears if you put things back.

Example. The three figures below show a fit on a test pattern. Newmod III calculated the DIMICA/TRIMICA model of Figure 1 at PA = 0.70 (R0, all other settings at their defaults), added counting noise and loaded it as the observed pattern. PA was then set back to 0.50, Show Difference was ticked, and Fit Model was run with the default ticks: PA, Reichweite A-B and Sigma* are the ones active with All Prop N = 1.

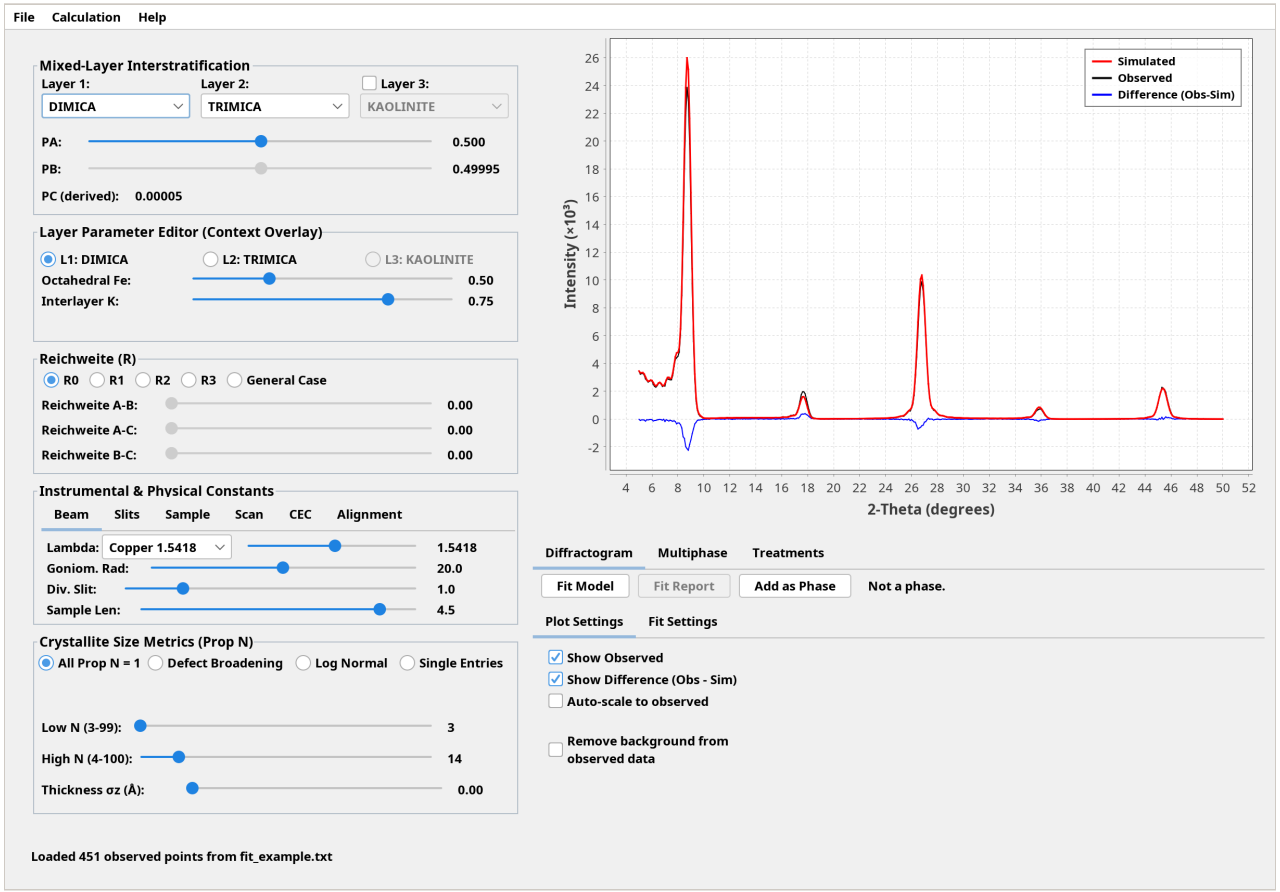


Figure 11. Before Fit Model: PA = 0.50 against a pattern made with PA = 0.70.

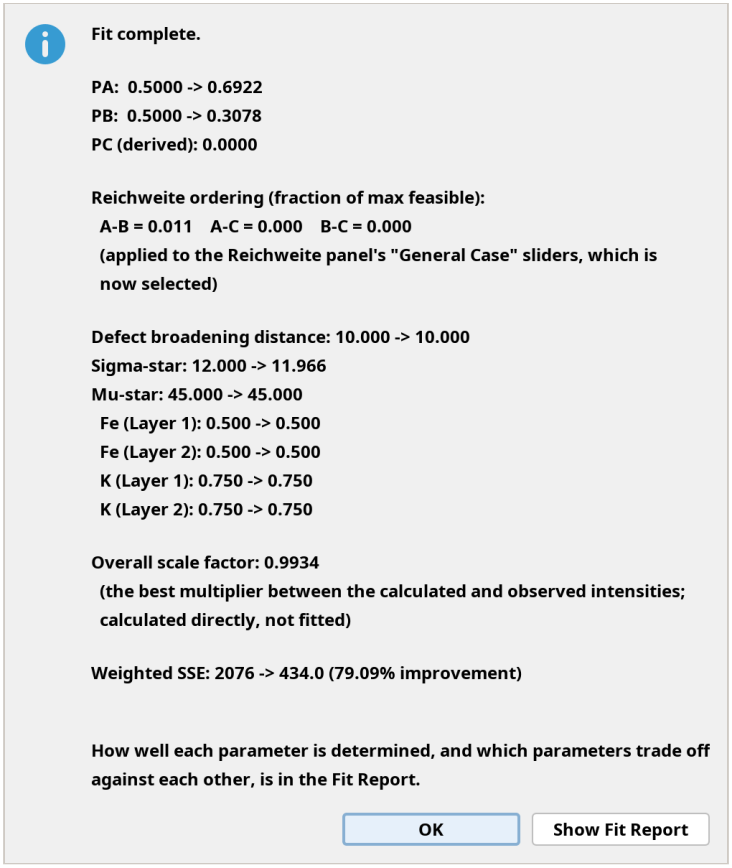


Figure 12. The summary at the end of the fit, with Show Fit Report.

The fit returned PA = 0.692 ± 0.005, Reichweite A-B = 0.01 ± 0.08 (consistent with the 0 of the R0 pattern) and Sigma* = 11.97 ± 0.09 against the true 12, with a reduced chi-square of 0.97: the misfit is close to the counting noise, and the difference curve is flat.

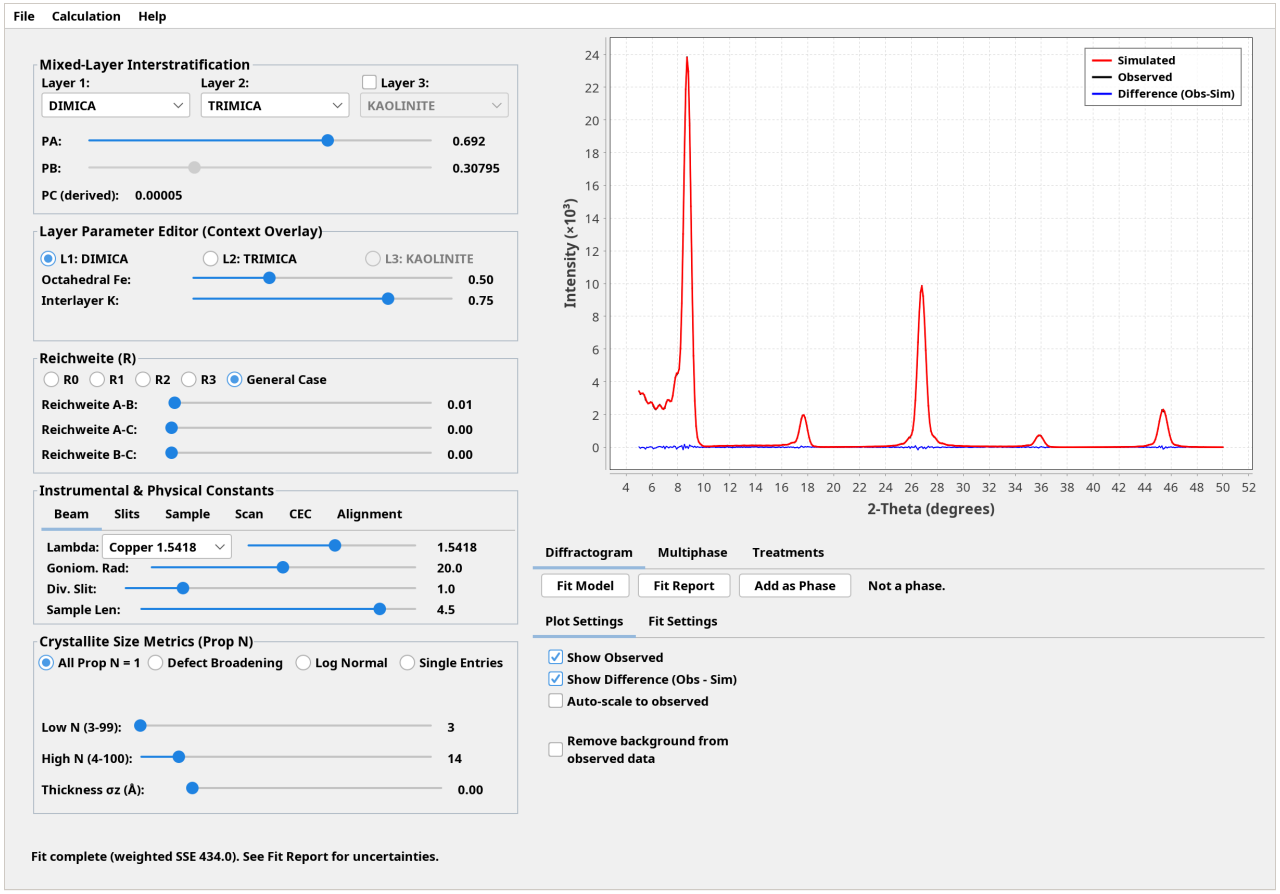


Figure 13. After Fit Model.

The Fit Report

A fit finds the best values; the Fit Report says how well the data pin 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. Fit Weights and Fit Models have a report of their own (section 12). **Copy** puts the whole report on the clipboard, **Save…** writes it to a `.txt` file, and **Close** closes the window.

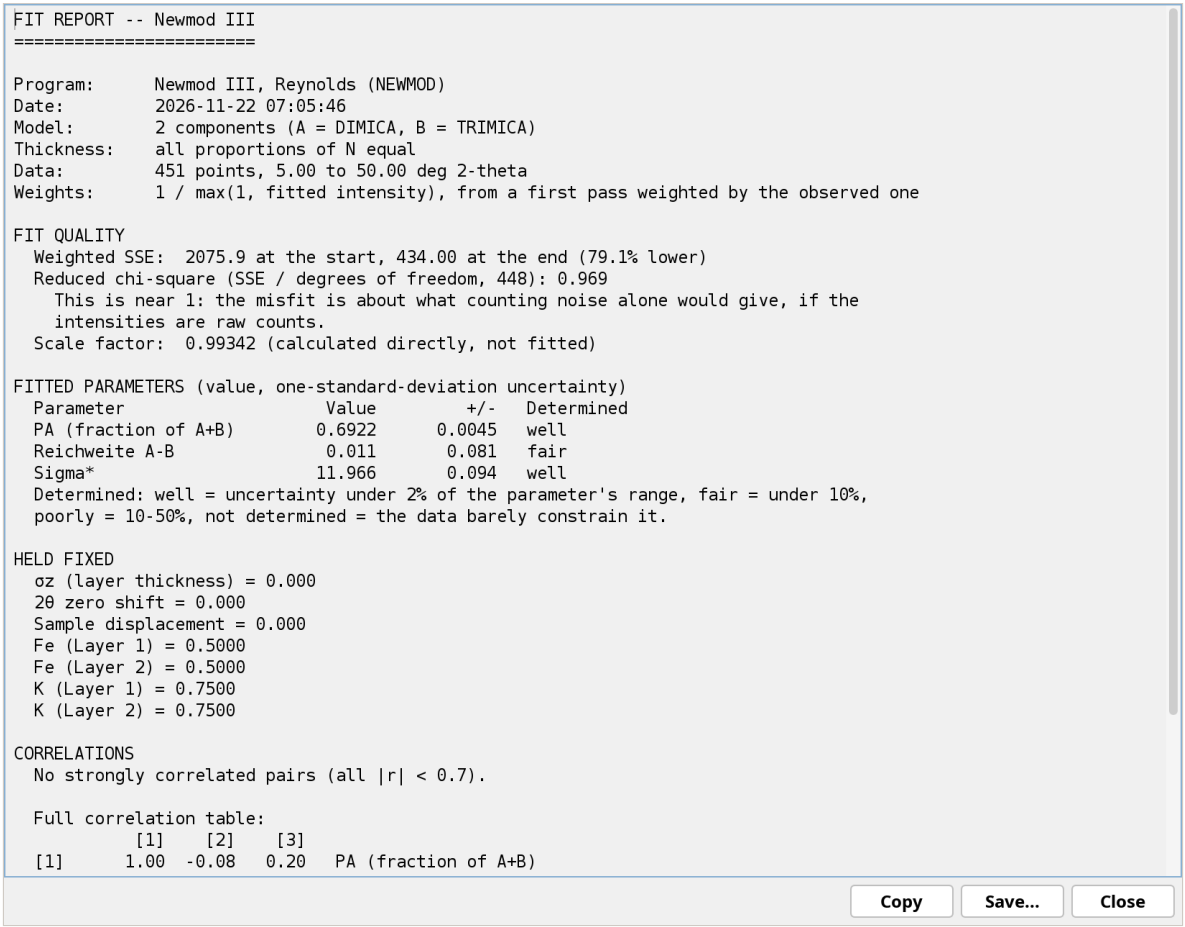


Figure 14. The Fit Report for the example above.

The report has five parts:

Part	What it says
Heading	Stacking method, date, layer types, thickness distribution, the points and 2θ range fitted, and the weighting
Fit quality	The weighted error at the start and end, the reduced chi-square (below) with what it means, and the scale factor
Fitted parameters	Each fitted value with its one-standard-deviation uncertainty (±) and how well it is determined, with flags
Held fixed	The parameters that could have been fitted but 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 parameter's fitted range: **well** means it is under 2 % of the range, **fair** under 10 %, **poorly** 10–50 %, and **not determined** means the data barely constrain it. Two flags warn that the number is less reliable: ***limit**, the value ended at the end of its range, so the best value may lie beyond it; and ***rough**, the error surface is uneven near the value (the slopes on either side differ), so the uncertainty may understate the real spread.

Reduced chi-square is the final weighted error divided by the degrees of freedom (points minus fitted parameters). 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, and the uncertainties are scaled up to allow for it; well below 1 usually means smoothed data or intensities that are not raw counts. Either way the uncertainties are scaled by the fit's own error, so they do not depend on the units of the intensities.

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 even if the fit looks good. 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 a little either side of its value (0.2 % of its range), which gives how the pattern changes with each parameter, J. With W the fit's weights and s^2 the final weighted error per degree of freedom,

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

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 you whether a different, distant set of values fits as well (start the fit from a few different places to check that). In tests on synthetic patterns with known noise, the reported ± values matched the actual scatter of repeated fits closely.

Checking sensitivity: which parameters to fit (new in Newmod III)

Newmod III can fit many parameters, but a pattern cannot pin down all of them at once. Some barely change the pattern, and some change it in the same way as another, so the two can trade off without changing the fit. Fitting such parameters makes the fit slower and the results less certain. The **Check Sensitivity…** button, below the Parameters to Fit ticks on the Fit Settings tab (Figure 10), tests each parameter in a few seconds and, in the **Suggest** column of its report, recommends which ones to fit. It needs observed data. It does not fit anything or change the model.

The check moves each parameter up and down by 5 % of its range, holding the others, recalculates the pattern, scales it to the data as a fit does, and measures how much the match changes. Parameters that cannot matter in the current model are not tested and are listed as **not used**, with the reason (for example Defect Distance without Defect Broadening, or Mu*, which only scales the whole pattern). 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 15).

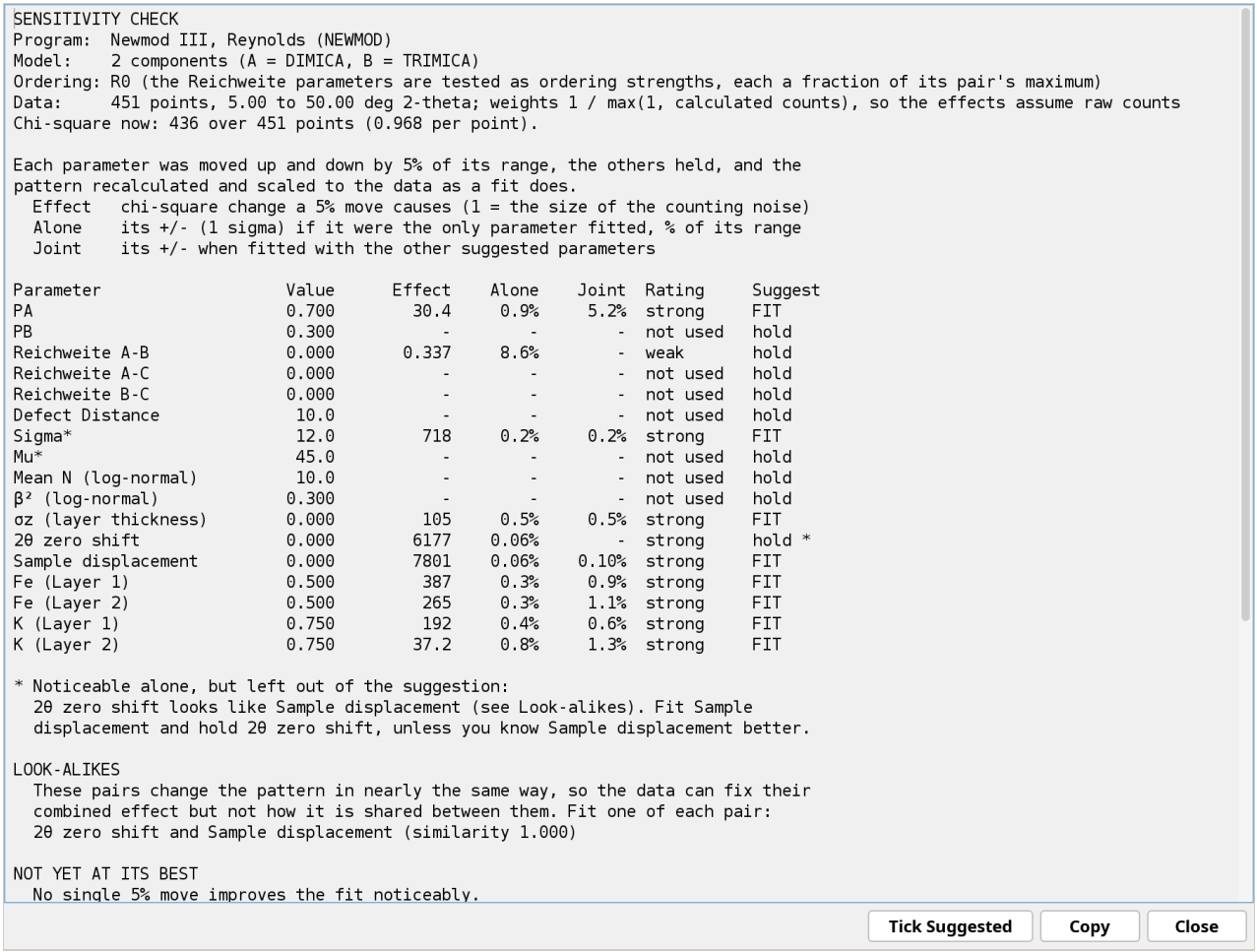


Figure 15. The sensitivity report for the test pattern of the example above, before any fit.

Column	What it says
Effect	The change in chi-square that a 5 % move causes. With raw counts, 1 is about the size of the counting noise: below 1, the data can hardly see the parameter.
Alone	The parameter's ± (one standard deviation) if it were the only one fitted, as a % of its 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 several times 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). The data can fix their combined effect but not how it is shared between them, so only one of each pair should be fitted. The 2θ zero shift and the sample displacement are the usual example: over a short 2θ range they shift the peaks almost identically, so the Suggest column marks only one of them **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: structure (proportions, ordering, crystallite size) first, then σz and the alignment terms, then the layer chemistry, since chemistry is often known from other analyses. **Not yet at its best** lists any parameter whose 5 % move already improves the fit 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, under Parameters to Fit, every parameter marked **FIT** in the Suggest column and untick all the others (Figure 16). 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.

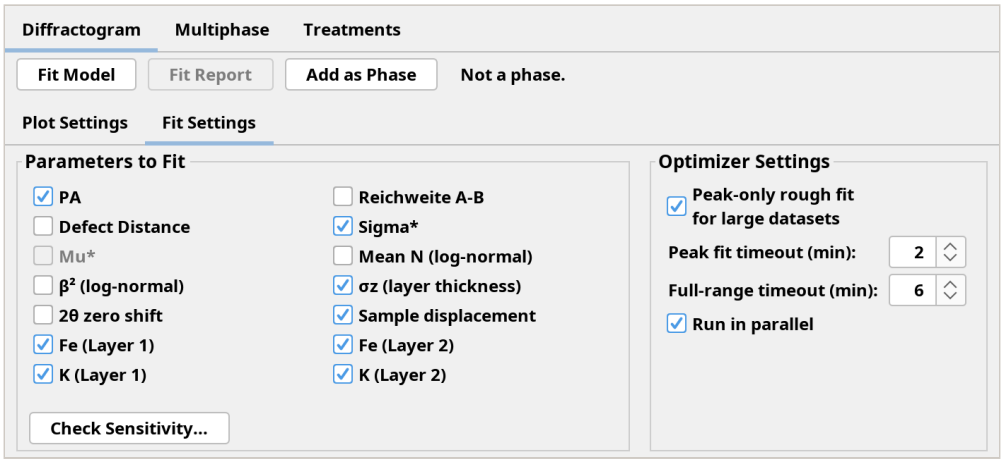


Figure 16. Parameters to Fit after pressing the Tick Suggested button.

Example. For the test pattern above (Figure 15), PA, Sigma* and σz are rated strong and marked **FIT** in the Suggest column, Reichweite A-B is weak (at R0 it has little to do), and the zero shift and sample displacement are flagged as look-alikes, so only the displacement is marked **FIT**. The layer chemistry is also marked **FIT** here because this synthetic pattern is free of the systematic errors of a real one. With measured data, chemistry often trades off with the proportions; the Suggest column then marks the chemistry **hold** and the proportions **FIT**.

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 discrete choices (layer types, the Reichweite level, the Prop N option). Like the Fit Report, it assumes the intensities are raw counts; it is not available in the multiphase view, where the button is hidden. In tests on synthetic patterns, the joint ± values agreed with the scatter of repeated fits to fresh noise within the expected sampling error.

12. Multiphase patterns

A multiphase pattern is the weighted sum of up to four stored patterns (phases), for samples that contain more than one mixed-layer or pure clay. It replaces Newmod 2's Multiphase analysis type. 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**.

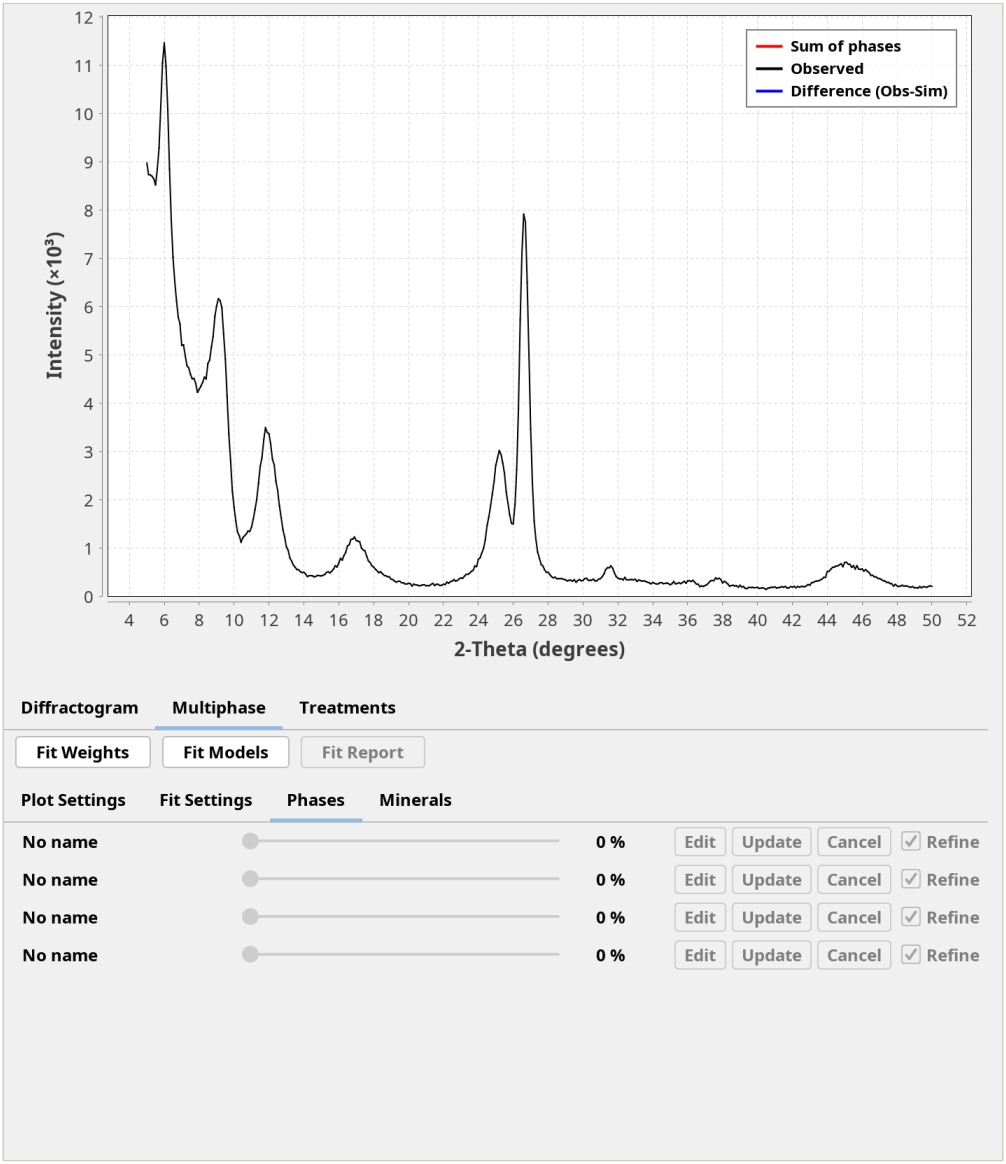


Figure 17. The multiphase view, with four empty phase slots.

Building a multiphase pattern

1. In the single-phase view (the **Diffractogram** tab), set up the first phase's model in the main panel.

2. Click **Add as Phase** and type a short name. The model's calculated pattern goes into the first slot whose weight is 0 %, and that slot's weight is set to 100 %. It is always stored unscaled, even when Auto-scale to observed is ticked: auto-scale fits each model to the data with its own factor, and storing that factor would make the weights incomparable between phases.
3. Change the model for the next phase and add it the same way. Repeat for up to four phases.
4. Open the **Multiphase** tab to see the weighted sum in red and, with **Show Observed** ticked on Plot Settings, the observed pattern in black. With **Show Difference (Obs - Sim)** ticked, the difference between them (observed minus the sum) is drawn in blue, as on the Diffractogram plot.

Each row on the Phases tab has these controls:

Control	What it does
Name	The name you typed. A ▶ and a highlight mark the phase now loaded in the main panel; the line beside Fit Model on the Diffractogram tab names it too.
Weight slider and %	The phase's weight in the sum, 0–100 %. Setting it to 0 % removes the phase and frees its slot.
Edit	Loads this phase's model back into the main panel so you can change it. Until you press Update or Cancel, every other row's buttons, Add as Phase and Fit Models are disabled.
Update	Replaces this slot's curve and model with the current model's calculated pattern (unscaled), 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 slot is left unchanged and the main panel goes back to the model it held before Edit.
Refine	Ticked: Fit Models refines this phase's model. Unticked: its model is kept as stored. Either way its weight is fitted.

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 that phase's own parameters, including the Fe and K of its own layer types; for a pure-mineral phase the PA, PB and Reichweite boxes are greyed out. A tick is stored in the phase at once and used by Fit Models; no Edit or Update is needed. Sigma* is greyed out because multiphase fits hold it (below), and Mu* is never refined. The 2θ zero shift and the sample displacement are greyed out too: they belong to the specimen and the instrument, which all phases share, so set them with Fit Model on one phase and keep the same values (Alignment tab) in every phase.

A multiphase pattern covers the 2θ range that all its phases share. All phases use the same scan range; changing Low, Hi or Step on the Scan tab changes it for every phase.

Fitting a multiphase pattern

Both buttons need observed data. Fit Weights needs at least one phase or reference mineral; Fit Models needs at least one phase and two components in all (reference minerals count). Both use the same weighting as a single fit, 1 / intensity in two passes (first the observed, then the fitted composite intensity), so weak features count as well as strong peaks.

Fit Weights adjusts the weights of all phases and reference minerals, and the background when **Fit background** is ticked on the Minerals tab, so their sum best matches the observed pattern. A phase's weight stays within its slider's 1–100 %; a reference mineral's weight has no upper limit. For reference minerals with **Fit** ticked it also fits their peak shift and width. The phase models are not changed.

Fit Models refines the models of the phases with Refine ticked, and fits the weights of all phases, reference minerals and the background as it goes, so the weights of everything that is not refined follow the changing models. Reference minerals keep their shift and width: run Fit Weights first to set those. Solving the weights is exact and takes no noticeable time; the time goes into recalculating the models. For each phase it refines the parameters ticked for that phase on Fit Settings, except Sigma*: in a multiphase pattern, Sigma* changes a phase's intensity almost uniformly and so trades against that phase's weight, which would leave the weights meaningless. Sigma* describes how the specimen is oriented, which all its phases share, so set it with a single-phase fit. It works in cycles:

1. All weights are solved together, so no phase starts against badly scaled neighbours.
2. The phases are refined one at a time, strongest first. Each is fitted against what the other phases, the reference minerals and the background leave unexplained.
3. After each phase, all weights are solved together again.
4. Cycles repeat until a cycle improves the fit by less than 0.1 %, or twelve cycles have run. Phases refined one at a time trade off against each other, so several cycles are usually needed before they settle.

If refining a phase would make the multiphase fit worse, that refinement is undone and the phase keeps its model; the summary says so. At the end the weight sliders show the fitted weights, relative to each phase's pattern as it was when the fit started. If a weight above 100 % is needed, every phase's pattern is multiplied by the same factor so that the strongest phase sits at 100 %, and the summary gives that factor. The summary also gives each phase's and each reference mineral's share of the total integrated intensity.

Click the button again while it runs to cancel. A summary at the end reports the result, and **Show Fit Report** in it opens the Fit Report (below). Like a single fit, a multiphase fit shows an out-of-date notice if you later add or update a phase, change a reference mineral, or change the window, the observed data or the background setting.

Example. In the figures below, the observed pattern was made by Newmod III from three phases: illite-smectite (DIMICA/DISMECTITE-2GLY, PA = 0.75), chlorite-smectite (TRI-TRICHLORITE/TRISMECTITE-2GLY, PA = 0.85) and kaolinite-smectite

(KAOLINITE/DISMECTITE-2GLY, PA = 0.90), all at R0, scaled to peak heights in the proportions 5 : 3 : 2, with a flat background of 150 counts and counting noise. The phases were then added with PA at 0.60, 0.70 and 0.78, the weights at 100 % and Refine ticked for all three, keeping the default ticks (PA and Reichweite A-B). Before the fit, the sum (red) misses the measured pattern (black) badly at 6° and between 10 and 32° 2θ, as the difference curve (blue) shows.

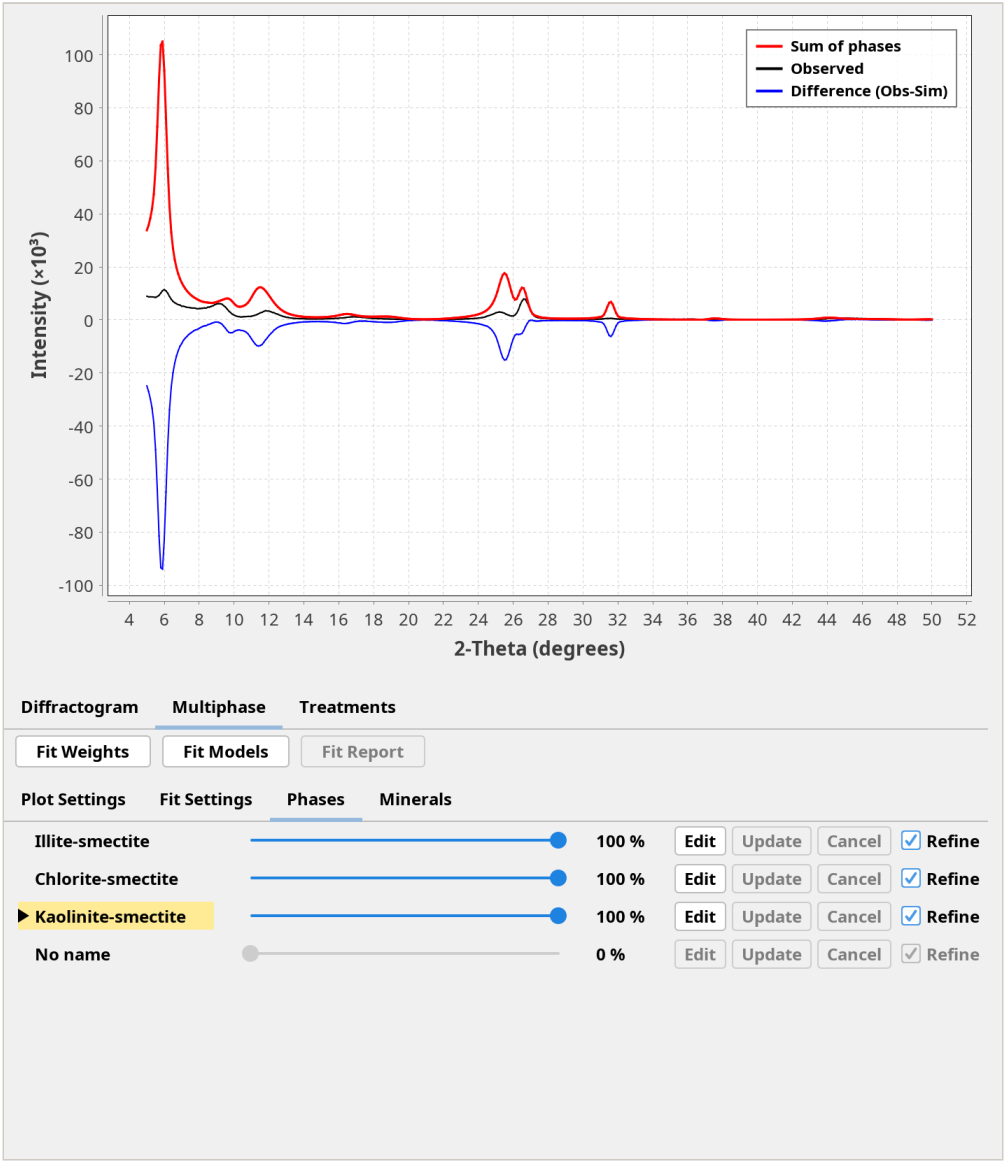


Figure 18. Before the fit: the perturbed phases against the measured pattern.

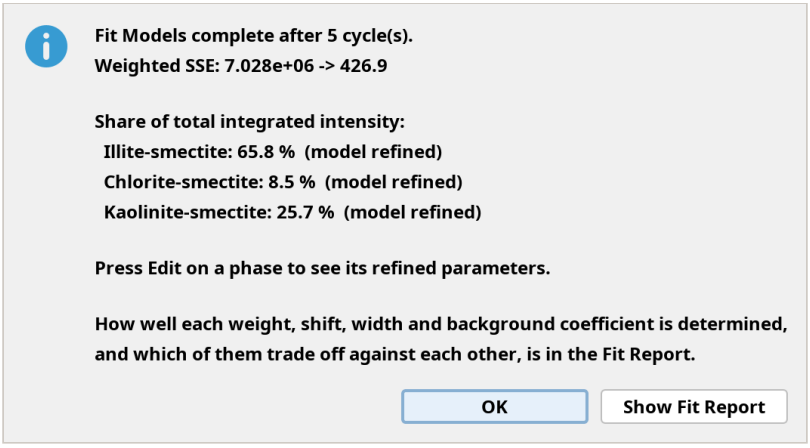


Figure 19. The summary at the end of Fit Models.

Fit Models finished after five cycles. The sum lies on the measured pattern, the difference curve is flat and the reduced chi-square in the Fit Report is 0.97, close to the 1 that counting noise alone gives. The weights, 79, 5 and 25 %, are proportions of each phase's calculated intensity, not of peak height, so they need not repeat the 5 : 3 : 2 used to make the pattern; the shares of integrated intensity in the summary are the better guide to how much each phase contributes. Refine only the parameters you need: parameters such as Fe and K change how strongly a phase scatters as well as the shape of its pattern, so with them free a slightly different model with a slightly different weight can reproduce the same sum, and the weights are less well pinned down. 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.

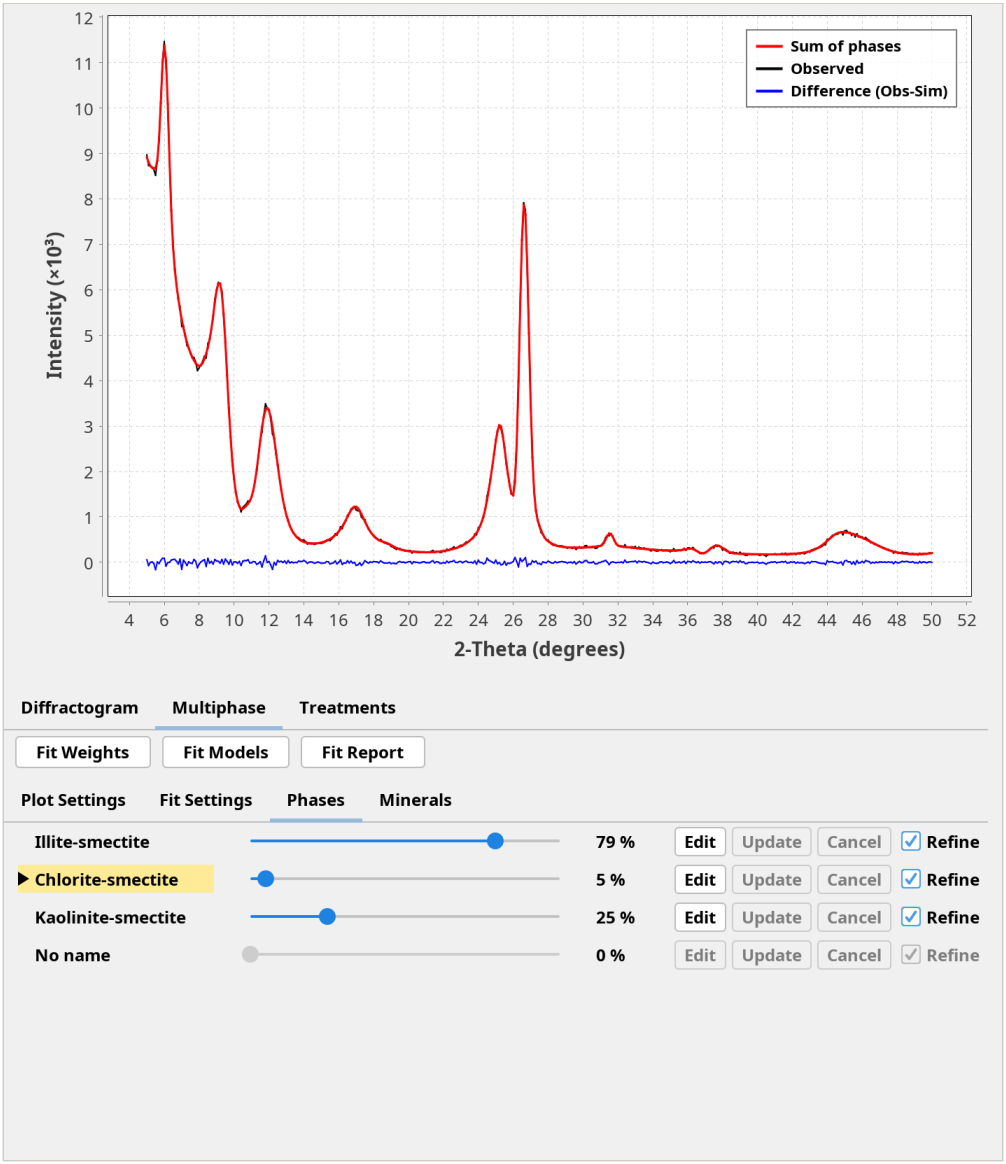


Figure 20. After Fit Models: the refined phases and weights.

The multiphase Fit Report

Fit Weights and Fit Models each publish a Fit Report, like Fit Model's (section 11). 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.

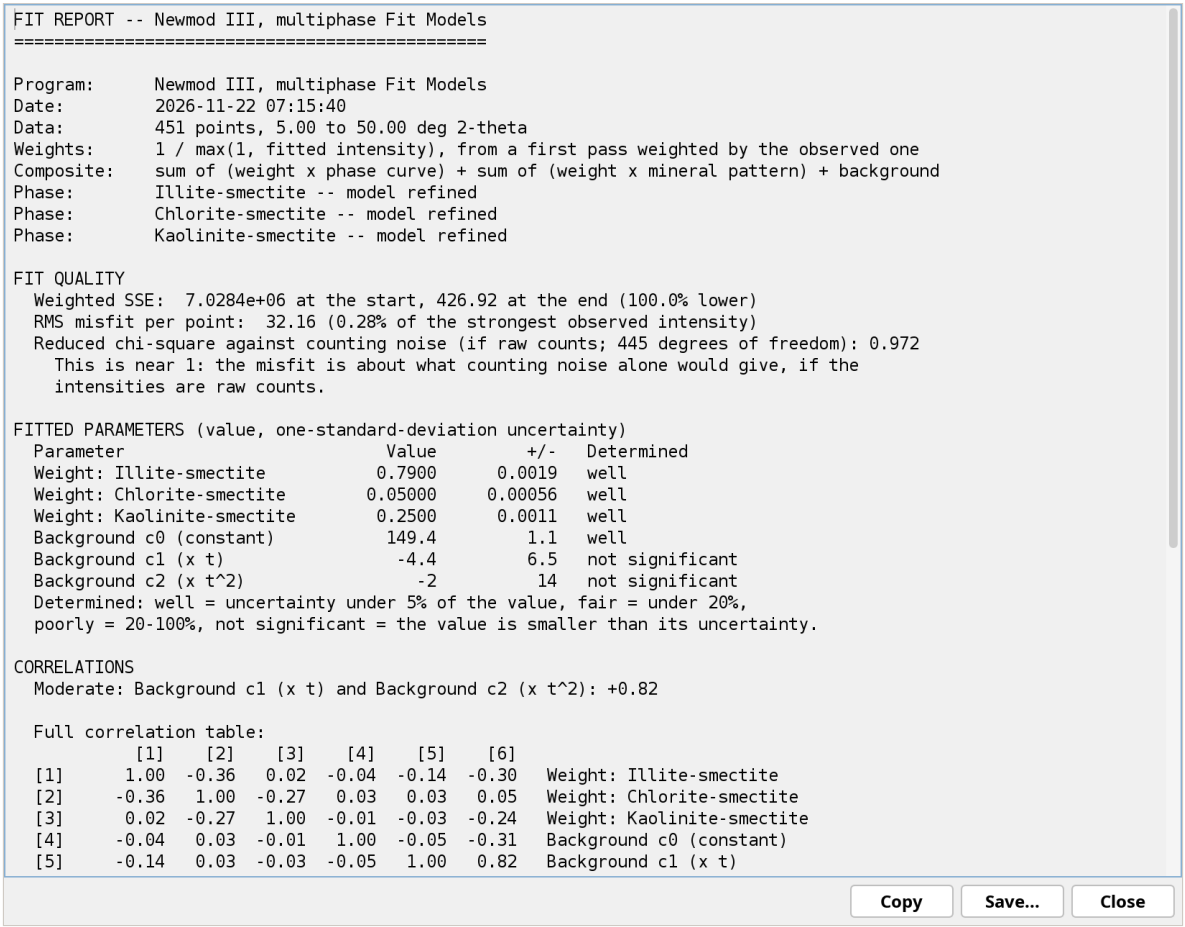


Figure 21. The Fit Report for the Fit Models example above.

Part	What it says
Heading	The fit (Fit Weights or Fit Models), date, the points and 2θ range compared, the weighting (1 / intensity, from the fitted composite, as in the fit's second pass), how the sum is made, and each phase (model refined or held) and each reference mineral
Fit quality	The weighted error at the start and the end; the RMS misfit per point; and the reduced chi-square against counting noise (section 11)
Fitted parameters	Each phase's weight, each reference 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

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; for a phase's own parameters, press **Edit** on it and run Fit Model, whose report covers them. The background is $c_0 + c_1 t + c_2 t^2$, with $t = (2\theta - 40°) / 40°$.

To keep a multiphase pattern, save a session (**File > Save Session...**); a model file holds only the displayed model.

Reference minerals (bulk powders)

A bulk-rock or soil sample is mostly quartz, feldspar, carbonate and the like, with clay a minor part. Newmod III calculates only the clays' 00l reflections, so on its own it cannot fit such a pattern. Reference minerals add the other minerals to the multiphase pattern: each has a fixed pattern of its own, scaled by a weight, and the clays, the minerals and a smooth background are fitted together. Open the **Minerals** tab in the multiphase view.

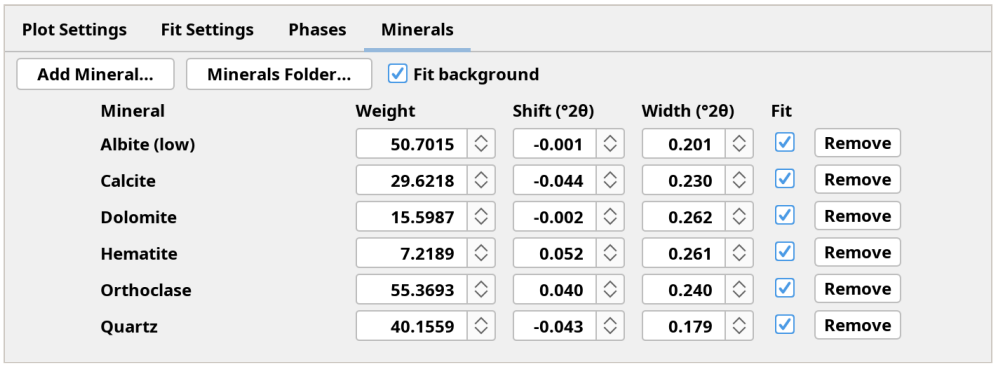


Figure 22. The Minerals tab with six reference minerals after Fit Weights.

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 the weight that best matches what the multiphase pattern leaves unexplained, at half strength.

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.
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 also fits this mineral's shift and width. A shift may move up to 0.25° per Fit Weights, 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, tick **Remove background** (Plot Settings) and set Low and Hi 2-Theta to the range you want fitted. Stay above the steep rise of the direct beam at low angles.
2. Add the clay 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 clay models, click **Fit Models**.

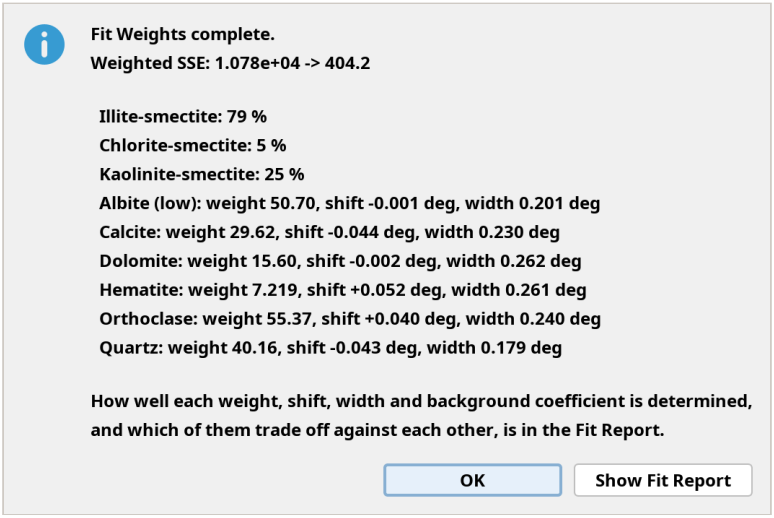


Figure 23. The summary at the end of Fit Weights with six reference minerals.

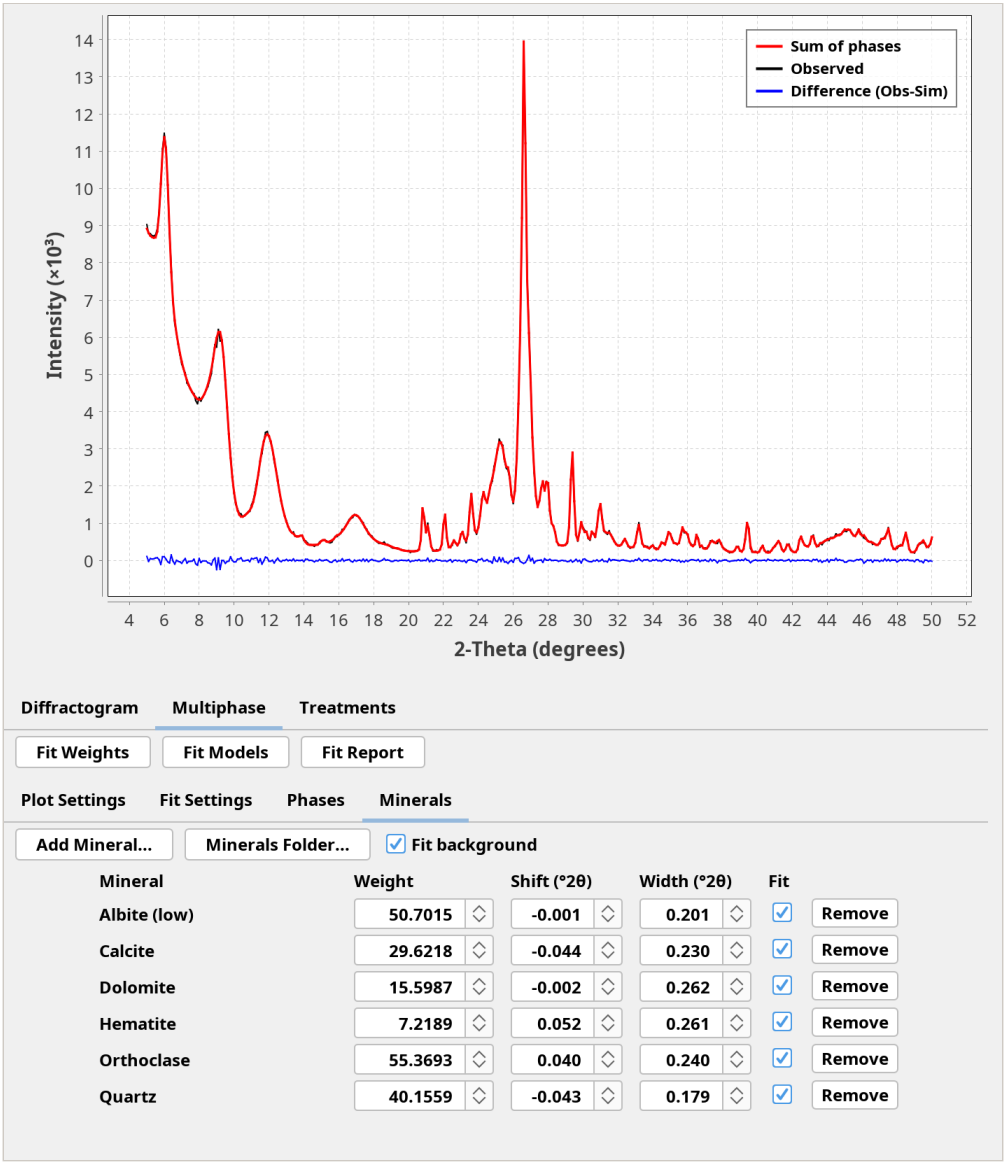


Figure 24. The example pattern of the previous figures with six minerals added, after Fit Weights.

In this example the observed 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 observed pattern, with every shift within 0.004° and every width within 0.01° of the values used to make the pattern, except the shift of hematite, the weakest mineral, which is 0.007° off.

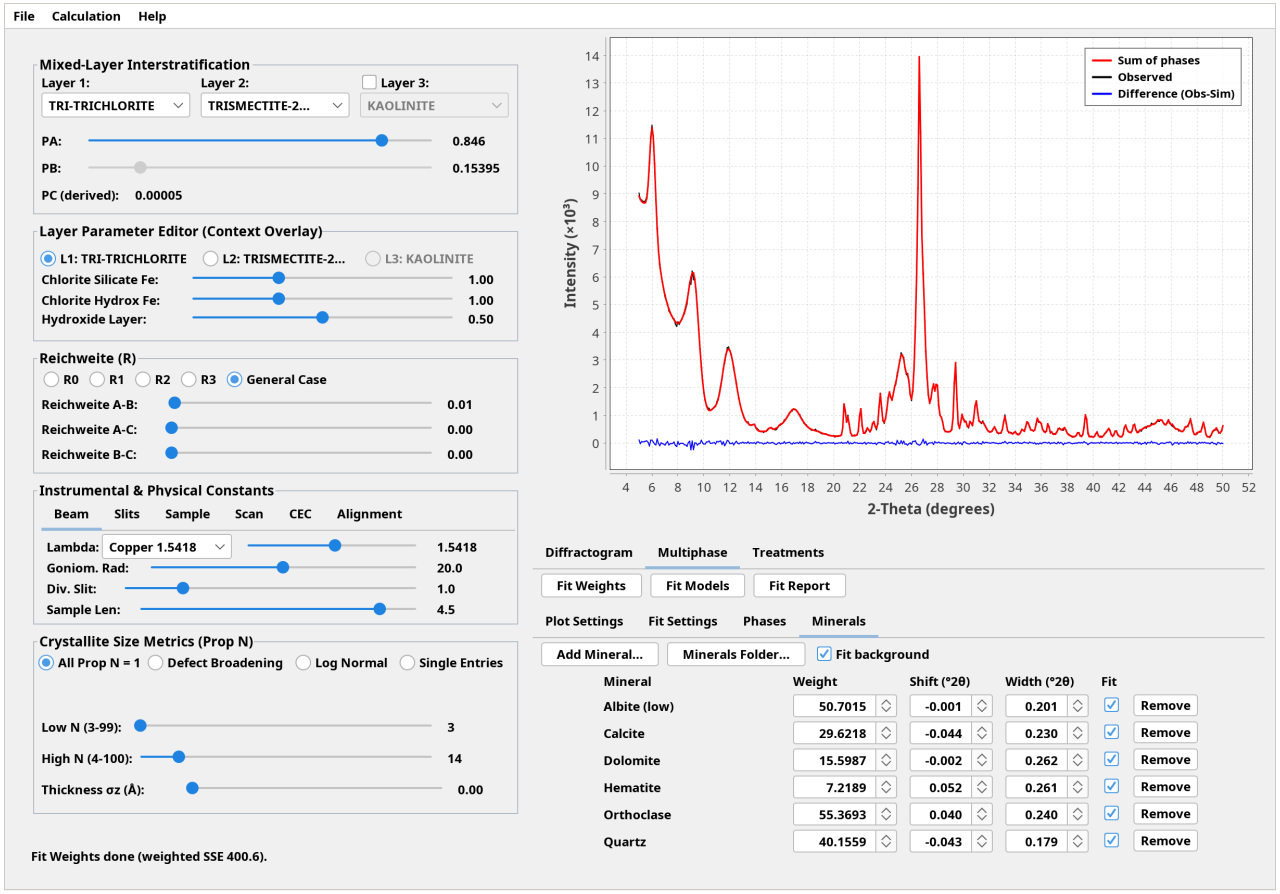


Figure 25. The main window in the multiphase view, with the Minerals tab.

Limits. Newmod III's clay calculation is for oriented aggregates. In a randomly oriented powder the clays' basal peaks are weaker relative to everything else, and their non-basal bands (near 4.5, 2.56 and 1.50 Å) are not calculated at all; minerals nearby may then take up that intensity by widening or shifting. Fit an oriented clay mount for the clay mineralogy, and keep the bulk fit for the non-clay minerals.

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

Group	Minerals
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)
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 on the Lambda slider, with Bragg-Brentano Lorentz-polarization and a pseudo-Voigt peak shape (40 % Lorentzian). The structure used for each mineral is listed in `SOURCES.txt` in the program's `minerals` resources and in the mineral list's description.

Your own minerals

Minerals Folder… opens your own minerals folder, `Documents\Newmod3C\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.

13. Several treatments of one sample (new in Newmod III)

A single pattern often cannot tell some parameters apart: the proportion of illite can trade off against the layer chemistry, or the ordering against the crystallite size, and still give much the same pattern. Different treatments of the same sample break those ties. Glycolation, a different exchange cation or heating changes the swelling layers, while the crystals themselves, their proportions, stacking order and thickness, stay the same. Only the right structure then fits every pattern. This is the multispecimen method of Sakharov, Lindgreen, Salyn and Drits (1999): *the structure of the sample is the one model that fits all its patterns*. The **Treatments** view fits one model to up to six patterns at once.

Preparing the patterns. Measure each treatment on the same oriented slide where possible (for example air-dried, then glycolated overnight, then heated), with the same slits, step and counting time. Then the orientation and thickness are the same in every pattern, as the joint fit assumes. Treatments cannot be simulated instead of measured: a calculated pattern contains only what the model already holds, and adds no information.

Setting up

1. Load the first pattern as usual (**File > Input Experimental Curve...**) and set up the model for it on the panel: layer types, proportions, ordering, crystallite size and chemistry. This pattern and the panel's model are row 1.
2. Click the **Treatments** tab below the plot. The plot now shows every pattern, stacked, with the model's pattern in red over each measured one (Figure 26).
3. On the **Treatments** tab, click **Add Pattern...** for each further treatment and choose its file.
4. In the table, set what the treatment changes: the state of each swelling layer and the exchange cation.

Column	What it holds
Show	Whether the pattern is drawn. Hidden patterns are still fitted.
Treatment	Its name, used in the plot and the reports. Click to edit.
File	The data file; row 1 is the pattern on the panel.
Layer A, B, C	Each layer type in this treatment. A smectite or vermiculite layer of the panel's model can take any state of the same kind: 2WAT, 1WAT, 2GLY, 1GLY or HEATED smectite, or vermiculite (dioctahedral with dioctahedral, trioctahedral with trioctahedral). Other layers are as on the panel. Newmod III guesses the state from the file name (*gly* or *EG*: 2GLY; *heat*, *300* or *550*: HEATED; *air* or *AD*: 2WAT); check it.
Cation	The exchange cation of this treatment. Row 1 uses the cation set on the panel's CEC tab.
χ^2/point	How well the model fits this pattern: about 1 for a fit within counting noise.
Zero shift	This pattern's fitted 2θ zero shift.

Remove removes the selected pattern (not row 1), and **Recalculate** redraws every pattern from the panel's current model, for example after moving a slider.

What is shared. Everything on the panel is shared by all the patterns: the proportions, the ordering, the crystallite size, Sigma*, σz and the chemistry, and the instrument settings, background removal and the Low–High window of the Scan tab. Only the swelling layers' state and the cation differ, as set in the table. Under **Fitted separately for each pattern** you can also give each pattern its own **2θ zero shift** and **sample displacement** (both ticked by default, since a slide is remounted between scans) and its own **σz** (glycolation or heating can make the swelling layers more or less uniform). Each pattern's scale is always its own.

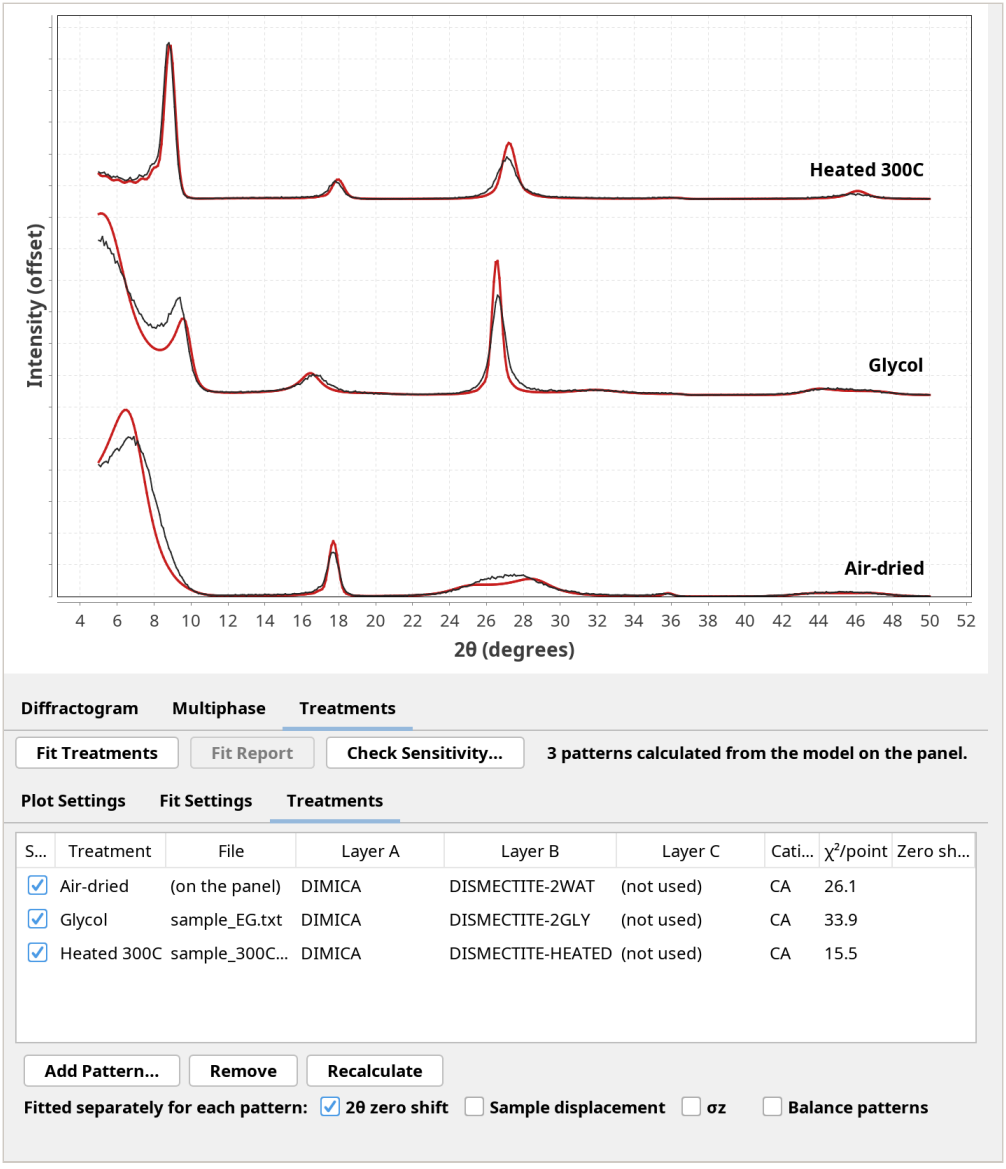


Figure 26. The Treatments view before the fit: air-dried, glycolated and heated patterns of one sample against a model with too little illite.

Fitting

Fit Treatments fits the parameters ticked on the Fit Settings tab to all the patterns at once, with the same optimizer, weights and time limit as Fit Model. The fit minimizes the sum of the patterns' weighted errors, which for raw counts is the correct joint likelihood. Click the button again to stop; the best point reached is kept. At the end the panel shows the fitted model with the values for row 1, and the table shows each pattern's χ^2 per point and zero shift (Figure 27).

Balance patterns. With raw counts, a pattern counted for longer counts for more in the fit, which is correct when the model can fit every pattern within its noise. If one pattern has a systematic misfit, for example from a background or a minor phase the model leaves out, it can then pull the shared parameters toward itself. With **Balance patterns** ticked, Fit Treatments fits once, weights each pattern by one over its own χ^2 per point, and fits again, so each pattern counts according to how well the model can fit it.

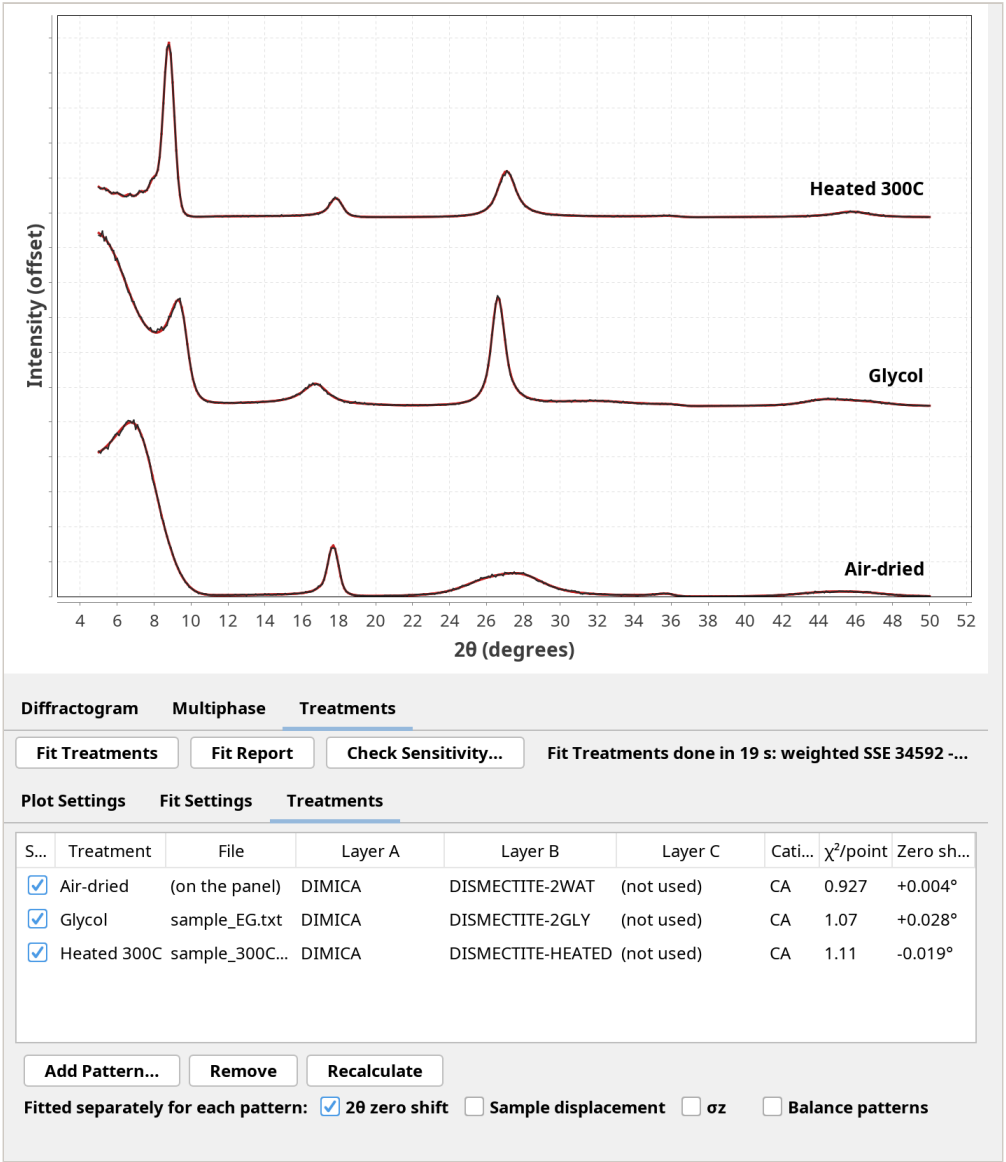


Figure 27. After Fit Treatments: one model fits all three patterns.

Example. The three patterns in Figures 26 and 27 were made by Newmod III from one illite-smectite (DIMICA/DISMECTITE, PA = 0.70, R0, σz = 0.30 Å, Ca) in three states: air-dried (2WAT), glycolated (2GLY) and heated (HEATED, at its default spacing of 9.60 Å), each with a different zero shift (0, +0.030 and −0.020°) and with counting noise (peaks about 5000 counts). The fit started from PA = 0.60 and σz = 0.10 Å, with PA, Reichweite A-B, Sigma*, σz, the heated spacing, the three Fe and K values and each pattern's zero shift ticked. It took about 20 seconds and found PA = 0.7002 ± 0.0010 and σz = 0.299 ± 0.002 Å, with zero shifts of +0.004, +0.028 and −0.019°, all within about one standard deviation of the true values; K came out at 0.751 ± 0.004 (true 0.75) and the heated spacing at 9.607 ± 0.007 Å. The χ^2 per point is 0.9–1.1 in each pattern.

The Fit Report and the sensitivity check

Fit Report opens the report on the last Fit Treatments (Figure 28). It has the same parts as the single-fit report (section 11), with these additions:

- The header lists each treatment: its layer states, cation, file, points and range.
- The fit quality gives each pattern's χ^2 per point. A pattern with a much larger value than the others is the one the shared model fits worst: its treatment may need another layer state, cation or a parameter of its own.
- A parameter fitted separately for each pattern carries the pattern's name in brackets, for example **2θ zero shift [Glycol]**.
- **What each pattern contributes** gives the ± of each shared parameter from all the patterns, and without each one in turn. A large rise without a pattern means that treatment pins the parameter down. In the example, leaving out the glycolated pattern raises the ± of PA from 0.0010 to 0.0015 and that of the smectite's Fe from 0.012 to 0.021, while leaving out the heated pattern changes little: for this sample, the glycol pattern adds most. Only the heated pattern determines the heated spacing, which is "not det." without it.

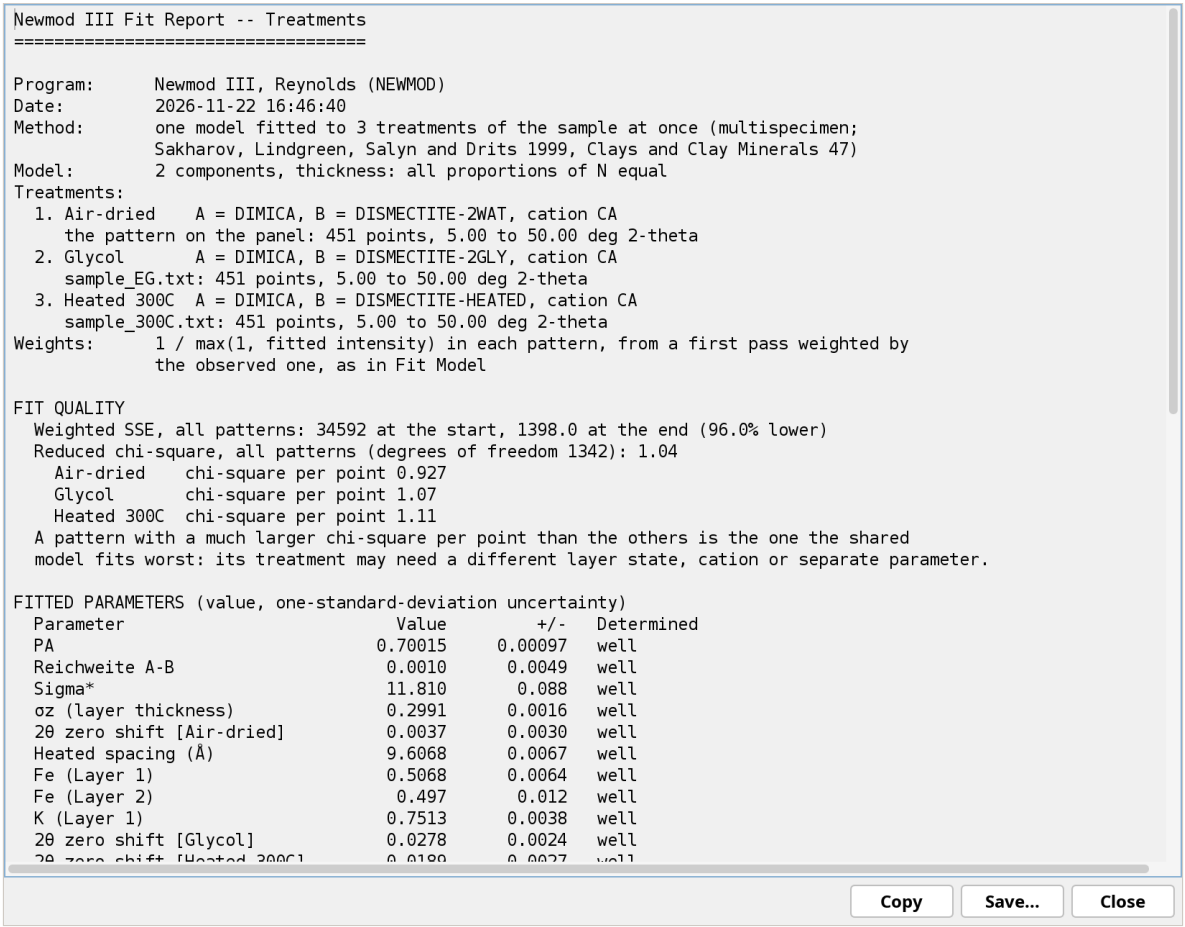


Figure 28. The Fit Report for the treatments example.

Check Sensitivity... in the Treatments view works as in section 11, on all the patterns together. Look-alike pairs from a single pattern often disappear when treatments are combined, and the joint ± values show what the set of patterns can determine before you fit. A parameter fitted for each pattern appears once per pattern; pressing the **Tick Suggested** button ticks it only if the Suggest column marks it **FIT** for every pattern, since one tick applies to all of them.

Limits

- Each treatment may change only the swelling layers' state and the cation; layer types of a different kind (smectite in one pattern, chlorite in another) are refused.
- Stacks of up to three layer types are possible, as on the panel. A sample that needs four (for example illite–smectite–two kinds of vermiculite) cannot be modelled.
- The Treatments view fits one model. A sample that needs a mixture of phases, as in the multiphase view, cannot yet be fitted across treatments.
- Sessions (**File > Save Session...**) keep the patterns, their settings and fitted values, with the data inside the file.

14. Worked example

This example repeats the Newmod 2 manual's illite/smectite simulation, then fits it to a measured pattern.

Simulate R1 illite/smectite

1. Start Newmod III. Leave **Layer 3** unticked (two-component mode).
2. Set **Layer 1** to DIMICA (illite) and **Layer 2** to DISMECTITE-2GLY (two-layer glycol smectite).
3. Set **PA** to 0.700. PB follows at 0.300.
4. In the Layer Parameter Editor, select **L1** and set Octahedral Fe to 0.10 and Interlayer K to 0.70. Select **L2** and set Octahedral Fe to 0.10.
5. In the Reichweite panel, select **R1**.
6. On the **Scan** tab, set Low 2-Theta to 2.00, Hi 2-Theta to 32.00 and Step to 0.02.
7. Leave everything else at its default. The pattern on the Diffractogram plot is the R1 illite/smectite with 70 % illite layers.
8. Save it with **File > Save Model Parameters…** (a `.nm3` file that restores this exact setup) or **File > Save Model Curve…** (a `.txt` file of 2θ and intensity for other programs).

Try R0 and General Case at A-B = 0.50 to see how ordering changes the low-angle reflections.

Fit it to a measured pattern

1. Load your measured pattern with **File > Input Experimental Curve…**. Low and Hi 2-Theta now match its range; narrow them if you want to fit only part of it.
2. On **Plot Settings**, tick **Auto-scale to observed** and **Show Difference (Obs - Sim)**. If the measured pattern has a sloping background, tick **Remove background from observed data**.
3. Adjust PA and the ordering by hand until the main peaks sit in roughly the right places.
4. On **Fit Settings**, tick PA, Reichweite A-B, Defect Distance and Sigma*, and the Fe and K values if you expect them to differ from your starting values.
5. Click **Fit Model** and watch the plot. When it finishes, read the summary, then check the difference curve for any systematic misfit.
6. Save the result with **File > Save Model Parameters…**; the observed pattern is saved in the same file.

15. Theory

Newmod III uses the same optical theory as NEWMOD and the earlier MOD-series programs (Reynolds and Hower, 1970; Reynolds, 1980), extended to three layer types. This summary is not comprehensive; readers new to the subject should study Reynolds (1980).

Diffracted intensity

The intensity equation used for the MOD-series programs applies only to layers that are centrosymmetric on projection to Z*. NEWMOD also handles the non-centrosymmetric kaolinite and serpentine layers, so all layers are treated as non-centrosymmetric, with the origin of each layer transform G at the centre of the lower-most oxygen plane of the tetrahedral sheet. This requires the general form of the angle-dependent intensity:

$$I = LP \sum_{S} G_j^* G_k \, \sigma_S \left(\cos \phi S + i \sin \phi S\right)$$

$$\phi = \frac{4\pi \sin \theta}{\lambda}$$

LP is the Lorentz-polarization factor. S is a spacing, in Å, defined by a number of layers stacked along Z. G^*_j is the complex conjugate of the transform of one layer type and G_k the transform of another; the subscripts identify the layer types separated by S. σ_S is the frequency of occurrence of the spacing S. It depends on the proportions of the layer types, the crystallite size distribution and the ordering defined by the Reichweite. The sum runs over all S, including S = 0 (single layers).

Lorentz-polarization factor

$$LP = \frac{\left(1 + \cos^2 2\theta\right) \psi}{\sin \theta}$$

The cosine term is the polarization factor, sin θ the single-crystal Lorentz factor and ψ the powder ring distribution factor. For a randomly oriented powder ψ is proportional to 1/sin θ; for a single crystal it is constant. Oriented clay aggregates lie between these (Reynolds, 1986). ψ depends on the root-mean-square angular divergence of the Soller slits and on σ*, the standard deviation of a Gaussian distribution of crystallite tilt (ω) from the mean orientation parallel to the sample surface:

$$\psi = \frac{\operatorname{erf}(Q)\sqrt{2\pi}}{2\sigma^* \bar{S}} - \frac{2 \sin \theta}{\bar{S}^2} \left(1 - e^{-Q^2}\right)$$

$$Q = \frac{\bar{S}}{2\sqrt{2}\, \sin \theta \, \sigma^*} \qquad \bar{S} = \sqrt{(S_1/2)^2 + (S_2/2)^2}$$

Here S_1 and S_2 are the two Soller slit divergences. ψ controls both the angle dependence and the absolute intensity, which is why well-oriented clay slides give much stronger patterns than poorly oriented or random aggregates. At moderate and high angles the absolute intensity is proportional to $1/(\sigma^*)^2$.

Absolute intensity

Calculated intensities I′ are put on an absolute basis I_0 (Reynolds, 1983):

$$I_0 = \frac{I' K \, d(001)}{\bar{N} V^2 \rho \mu^*} \qquad \sum_N P(N) = 1 \qquad \bar{N} = \sum_N P(N)\, N$$

d(001) is the weighted mean basal spacing of the components, V the weighted mean unit cell volume, ρ the density, μ* the mean mass absorption coefficient and $\bar{N}$ the mean of the crystallite size distribution. K combines physical constants, an empirical constant and the quartz reference intensity, which accounts for the instrument's operating conditions. The quartz measurement must be made under the same conditions as the clay patterns being compared. Overall errors are about 10 % if μ* and σ* are known (Reynolds, 1986). For most quantitative work, intensity ratios between calculated minerals are used instead, and these are accurate enough to serve as standards.

Short-sample correction

At low angles the beam footprint can be longer than the sample. Its length is

$$LB = \frac{R_0 \, \alpha \, (\pi/180)}{\sin \theta}$$

where R_0 is the goniometer radius in cm and α the divergence slit in degrees. Where LB exceeds the sample length, intensities are multiplied by the sample length and divided by LB. The theta-compensating slit option bypasses this: all intensities are multiplied by sin θ and normalized to the standard geometry at 26.65° 2θ.

Structures of the component layers

The layer transforms G are Fourier transforms of the atomic structure along Z. Unit cell volumes are based on the half cell $(Si, Al)_4O_{10}$, except for the 1:1 minerals, which use Si_2O_5. Atomic scattering factors follow Wright (1973): half-ionized for Si, Al and silicate O, fully ionized for other cations. Water, ethylene glycol and OH^- scattering is the sum of the neutral-atom factors for H^+ and O^{2-}. Debye-Waller corrections use B = 1.5 for cations, B = 2 for anions, and B = 11 for glycol and some of the water in two-layer water smectite.

There are three 2:1 silicate layer structures. The dioctahedral layer, from unpublished work by Bridges and Reynolds on illite, is used for all dioctahedral components except smectite, which follows Reynolds (1965). All trioctahedral 2:1 layers follow Mathieson and Walker (1954) for vermiculite. Kaolinite coordinates are those of Zvyagin (1960), and serpentine has the generalized 1:1 trioctahedral structure of Bailey (1969).

Mineral component	Al per 4 tetrahedral sites
Illite	0.5
Biotite	1.0
Di-smectite	0.0
Tri-smectite	0.35
Vermiculite	1.0
Chlorite	1.0
Kaolinite	0.0 (per Si_4O_{10})
Serpentine	0.0 (per Si_4O_{10})

The Si/Al ratio has only small effects on intensity but is included for completeness.

Interlayer structures are computed separately and added to the silicate layer transform. Two-layer ethylene glycol follows Reynolds (1965) and one-layer Na glycol Bradley, Weiss and Rowland (1963). Two-layer water smectite is from unpublished work by Hower and Reynolds. One-layer water smectite places the cations and water at the centre of the interlayer, with water content from Mooney, Keenan and Wood (1952). The trioctahedral chlorite hydroxide layer follows Brindley (1961A); the dioctahedral one has the Al-OH separation of a generalized kaolinite (Brindley, 1961B). Two-layer water vermiculite follows Mathieson and Walker (1954).

Some interlayer structures are educated guesses. Small errors in atomic positions cause only small intensity errors at the low and intermediate angles of most clay work. At 50° 2θ (CuKα) and above, results are accurate only for the better-known components: illite, biotite, two-layer glycol smectite, two-layer water vermiculite, tri-trichlorite and kaolinite.

Ordering for two components

For two components, ordering follows Markovian (conditional) probability, with A the more abundant layer type and PA + PB = 1. PB.A is the probability that an A follows a B, and PB.A + PB.B = 1.

- PB.A = PA: the type of each layer is independent of the one before; random interstratification, R = 0.
- PB.A = 0: approximately a physical mixture of A and B.
- PB.A = 1 (R = 1): no BB pairs, every B is followed by an A. At PA = 0.5 this describes the rectorite, corrensite and allevardite structures.

Longer-range ordering also depends on the layers beyond the nearest neighbour. With PB.A = 1, setting PBA.A = PA.A keeps R = 1, while PBA.A = 1 forbids the sequence BAB, so B layers are separated by at least two A layers: R = 2. Likewise PBAA.A = 1 gives R = 3 by forbidding BAAB. R = 2 requires PA of at least 0.667, and R = 3 requires PA of at least 0.75. Parameters that do not describe a possible structure give negative probabilities, reported as Nonsense ordering.

The domain statistics for two components were computed with the fast recursive algorithm of Bethke and Reynolds (1986).

Ordering for three components (new in Newmod III)

Bethke's closed-form equations apply only to two layer types, so Newmod III builds the ordering differently. The stacking is a reversible Markov chain over the three layer types whose long-run proportions are exactly PA, PB and PC. Each pair of layer types has its own ordering strength, from random (0) to the most alternation the proportions allow (1); for two components this reduces to Newmod 2's single Reichweite, and A-B = 0.5 reproduces its R = 0.5. R2 and R3 add second- and third-order dependence; at every order the probabilities sum to 1 and reduce exactly to the order below (Sakharov and Lanson, 2013). The one probability R3 leaves free is set to depart least from R2 (minimum relative entropy; Kullback and Leibler, 1951); for two components this is Bethke and Reynolds' R3. Domain frequencies are then counted directly from the chain.

Summation methods (new in Newmod III)

The sum over spacings S in the intensity equation can be evaluated in two ways, chosen from the **Stacking Method** menu (section 4). Both use the same layer transforms, ordering, crystallite size distribution and Lorentz-polarization factor, and give the same pattern.

Reynolds. The domain frequencies σS are tabulated once, as described above, and the phase factor of every domain is summed at each angle.

Kakinoki–Komura. Following Kakinoki and Komura (1952, 1965) and Drits and Sakharov (1976), as presented by Drits and Tchoubar (1990), the ordering is written as a matrix **P** of transition probabilities between states, a state being the last R layers of the stack. Multiplying each transition by the phase factor of the layer it adds turns the sum over all stacks into powers of one matrix, so the domain compositions never have to be listed. For crystallites of N layers

$$I = LP\,\mathrm{Re}\,\mathrm{Spur}\left[\mathbf{F}\,\mathbf{W}\left(\mathbf{I} + 2\sum_{n=1}^{N-1}\frac{N-n}{N}\,\mathbf{Q}^{n}\right)\right]$$

$$\mathbf{Q} = \mathbf{P}\,\mathbf{\Phi} \qquad \Phi_{jj} = e^{i\phi d_j}$$

where **W** holds the abundances of the states, **F** the products $G^*_j G_k$ of the layer transforms, d_j the basal spacing of layer type j, and Spur is the trace; the result is averaged over the crystallite size distribution P(N). The work grows with the number of states (27 for R3), not of domain compositions; the two methods agree to about 10^{-13}.

Layer-thickness fluctuation σz (new in Newmod III)

If each spacing between neighbouring layers varies about its mean by a normally distributed amount with standard deviation σz, independently of the other spacings (Drits and Tchoubar, 1990), then averaging over those variations multiplies the

contribution of every spacing S in the intensity equation by

$$D^{\,m} \qquad D = \exp\!\left(-\tfrac{1}{2}\,\phi^2\sigma_z^2\right)$$

where m is the number of layer-to-layer spacings that make up S (m = 0 for single layers, which are unaffected). Because D falls with angle and is raised to the power m, distant layer pairs stop reinforcing each other first at high angles: the peaks broaden and weaken increasingly with 2θ, while their positions do not move. In the Kakinoki–Komura form the same factor is included by writing $\Phi_{jj} = D\, e^{i\varphi d_j}$; both summation methods apply it identically, and σz = 0 (D = 1) gives the original calculation.

Zero shift and sample displacement (new in Newmod III)

A zero error z_0 moves every reflection by the same amount. A sample surface displaced by s from the goniometer axis moves a reflection at angle θ by (Klug and Alexander, 1974)

$$\Delta 2\theta = \frac{2\,s\cos\theta}{R} \quad \text{(radians)}$$

where R is the goniometer radius (Goniom. Rad.), with s positive for a surface above the axis. Newmod III calculates the intensity reported at the scan angle 2θ from the angle $2\theta - z_0 - \Delta 2\theta$, so a peak calculated at 2θ appears at $2\theta + z_0 + \Delta 2\theta$; everything else in the calculation, including the Lorentz-polarization factor and the short-sample correction, uses that shifted angle. Both summation methods apply it identically, and $z_0 = s = 0$ gives the original calculation.

Several treatments (new in Newmod III)

For K patterns of one sample, Fit Treatments minimizes

$$\chi^2(\mathbf{p}) = \sum_{k=1}^{K} b_k \sum_i w_{ki}\left(y_{ki} - s_k\, I_k(2\theta_{ki};\, \mathbf{p}_{\text{shared}}, \mathbf{p}_k)\right)^2$$

where y_{ki} are pattern k's counts, w_{ki} its weights (1 / max(1, y_{ki}) in a first pass, then 1 / max(1, $s_k I_k$) from the fitted patterns, as for one pattern), I_k its calculated pattern for its own layer states and cation, s_k its scale (solved exactly at every step), $\mathbf{p}_{\text{shared}}$ the parameters common to all patterns and $\mathbf{p}_k$ those fitted for pattern k alone (zero shift, displacement, σz when chosen). The balance factors b_k are 1, or with Balance patterns one over pattern k's χ^2 per point after a first fit. The uncertainties follow as for one pattern (section 11) from the Jacobian of all the patterns stacked together, so the information from the treatments adds:

$$\operatorname{cov}(\mathbf{p}) \approx s^2\left(\sum_k J_k^{\mathsf{T}} W_k J_k\right)^{-1}$$

The table of what each pattern contributes repeats this calculation with one pattern's rows (and its own parameters) left out, at the same s^2. Treatments help most when they change the pattern in different directions: then the J_k are unlike one another and the sum is far better conditioned than any one term, which is how a second treatment can separate parameters that trade off in a single pattern.

16. Reference: layer types and advanced techniques

Newmod III offers the 18 layer types of Newmod 2 and two new ones for heated smectite, with the basal spacings and layer areas built into the calculation.

Layer type	Mineral	d(001), Å	Area, Å²	Chemistry sliders
DIMICA	Illite (dioctahedral mica)	9.98	46.8	Fe 0–1.7, K 0–1
TRIMICA	Biotite (trioctahedral mica)	10.00	49.0	Fe 0–3, K 0–1
DISMECTITE-2GLY	Di-smectite, two-layer glycol	16.9	46.8	Fe 0–1.7
DISMECTITE-1GLY	Di-smectite, one-layer glycol (Na)	12.9	46.8	Fe 0–1.7
TRISMECTITE-2GLY	Tri-smectite, two-layer glycol	16.9	49.0	Fe 0–3
TRISMECTITE-1GLY	Tri-smectite, one-layer glycol (Na)	12.9	49.0	Fe 0–3
DISMECTITE-2WAT	Di-smectite, two-layer water	15.0	46.8	Fe 0–1.7
TRISMECTITE-2WAT	Tri-smectite, two-layer water	15.0	49.0	Fe 0–3
DISMECTITE-1WAT	Di-smectite, one-layer water	12.4	46.8	Fe 0–1.7
TRISMECTITE-1WAT	Tri-smectite, one-layer water	12.4	49.0	Fe 0–3
DIVERMICULITE	Di-vermiculite, two-layer water	14.32	46.8	Fe 0–1.7
TRIVERMICULITE	Tri-vermiculite, two-layer water	14.32	49.0	Fe 0–3
DI-DICHLORITE	Chlorite, di 2:1 layer, di hydroxide	14.15	46.8	Silicate Fe 0–2, Hydrox Fe 0–2, Hydroxide Layer 0–1
TRI-TRICHLORITE	Chlorite, tri 2:1 layer, tri hydroxide	14.2	49.0	Silicate Fe 0–3, Hydrox Fe 0–3, Hydroxide Layer 0–1
DI-TRICHLORITE	Chlorite, di 2:1 layer, tri hydroxide	14.2	46.8	Silicate Fe 0–2, Hydrox Fe 0–3, Hydroxide Layer 0–1
TRI-DICHLORITE	Chlorite, tri 2:1 layer, di hydroxide	14.15	49.0	Silicate Fe 0–3, Hydrox Fe 0–2, Hydroxide Layer 0–1
KAOLINITE	Kaolinite	7.15	44.1	none
SERPENTINE	Serpentine	7.1	49.0	Fe 0–3

Layer type	Mineral	d(001), Å	Area, Å²	Chemistry sliders
DISMECTITE-HEATED	Di-smectite, collapsed by heating (new)	9.6 (adjustable)	46.8	Fe 0–1.7
TRISMECTITE-HEATED	Tri-smectite, collapsed by heating (new)	9.7 (adjustable)	49.0	Fe 0–3

Heated smectite (new in Newmod III). Heating to about 300–550 °C drives out the interlayer water and collapses smectite layers to about 10 Å; only the exchange cation is left, on the interlayer mid-plane. The two HEATED types model such layers, typically as the third treatment of a sample (section 13). Unlike the other layer types, whose spacings are fixed as in NEWMOD, the heated spacing varies from sample to sample with the exchange cation and the heating (from about 9.5 Å to about 10.0 Å with K), so it is a setting, **Heated d(001)** on the CEC tab, and can be fitted (**Heated spacing** on the Fit Settings tab). Its defaults come from the USGS reference patterns of oriented mounts heated to 400 °C (Poppe et al. 2001): read from their 001 and 002 peaks and corrected for the thin-crystal shift of the 001 by Newmod III's own calculation, the montmorillonites (API 11 and 25) and the nontronite give 9.55–9.65 Å, hence 9.6 Å for dioctahedral smectite, and the saponite about 9.7 Å. It matters: in a test on a heated illite-smectite pattern alone (70 % illite, true spacing 9.55 Å), holding the spacing 0.05 Å too high gave 65 % illite, and 0.15 Å too high 55 %. Fit it, or set it from a pure smectite heated the same way, when the heated pattern is to determine the proportions. A collapse that is incomplete, with some layers still holding water, can be modelled by a third component (for example DISMECTITE-1WAT).

Iron is given a small anomalous-dispersion correction for copper (wavelengths 1.5–1.6 Å) and cobalt (1.7–1.8 Å) radiation; other wavelengths get none.

Advanced techniques from Newmod 2

The Newmod 2 manual described ways to model minerals that are not on the list. Their status in this version:

Technique	Newmod 2 method	In Newmod III
Pure minerals	Set both layer types the same; use R = 0	Works as before; the layers now share their chemistry, and the proportions and Reichweite are greyed out (section 5)
Talc-saponite, pyrophyllite	Biotite or illite with K = 0 and d(001) changed to 9.33 or 9.2 Å	Not possible: d(001) cannot be changed
Ammonium illite, paragonite	Illite with K = 0.56 (10 electrons in place of 18) and d(001) changed to 10.32 or 9.66 Å	The K value can be set; d(001) cannot be changed
Other exchangeable cations (Cs, Rb, Pb, Zn)	An electron-equivalent value of a standard cation	Only where the equivalent amount fits the Exchange Cap range (0.250–0.450)

Technique	Newmod 2 method	In Newmod III
Unusual octahedral cations (Zn, Li-rich cookeite, lepidolite)	A fictitious Fe value, possibly above the normal maximum or negative	Only within the Fe slider ranges (0–1.7 or 0–3); values outside them cannot be entered

The ammonium-illite approach works because, at low and intermediate angles, a scattering factor is proportional to the number of electrons: NH_4^+ has 10 and K^+ 18, so 10/18 = 0.56 K mimics the NH_4^+ scattering. Exotic compositions also give wrong molecular weights, and so wrong absolute intensities. If absolute intensities matter, multiply calculated intensities by (molecular weight used by the program) / (correct molecular weight). Relative intensities within one pattern are much more reliable.

17. Support, license and references

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

Comment. Newmod III is a tool for teaching and research. No claim is made that it is a strictly correct model for mixed-layered clays, but some forty years of experience with the MOD-series programs and NEWMOD, by many investigators, has shown the usefulness of this mathematical-physical approach.

License and disclaimer. Newmod III 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 Newmod3C... > Licenses...**.

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