

Petrolog v. 3

Manual

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The latest version of Petrolog and this manual can be downloaded from the Petrolog home page at <http://petrolog.web.ru>

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1. Overview of Petrolog3

Petrolog3 is software for modeling fractional and equilibrium crystallization and reverse of fractional crystallization at variable pressure, melt oxidation state and melt H₂O contents, and for modeling post-entrapment re-equilibration of melt inclusions in olivine.

Modeling of crystallization in Petrolog3 is based on the concept of pseudo-liquidus temperatures (Nathan, Vankirk, 1978; Nielsen, Dungan, 1983; Ariskin et al., 1986). The method relies on the ability of the mineral-melt equilibria models to calculate liquidus temperature not only for the range of melt compositions where the minerals are stable, but also in the metastable regions of melt compositions for each phase (i.e., pseudo-liquidus temperatures).

The essence of the technique is to compare calculated pseudo-liquidus temperatures for a number of minerals that may crystallize from a given melt composition. The mineral with the highest calculated temperature is the mineral on the liquidus of the melt, and this mineral is subtracted from melt, after which the process is repeated. Calculated temperatures for non-liquidus minerals are pseudo-liquidus temperatures, as these minerals are not actually on the liquidus of the melt.

Petrolog3 offers a model-independent algorithm, which can incorporate a potentially unlimited number of mineral-melt equilibria models for major and trace elements; and of models describing melt physical parameters, such as density and viscosity, solubility of fluid components in silicate melts, melt oxidation state.

Note: Mineral-melt equilibrium models that can be included in Petrolog3 must calculate, for a given melt composition at a given pressure and oxidation state, both the temperature at which the mineral appears on the liquidus of this melt, and the composition of the mineral.

Petrolog3 runs under Windows operating system (XP or higher). Screen resolution should be set to higher than 800x600 pixels.

Note: Petrolog3 requires that the DPI setting of Windows operating system is set to 'Normal size' at Display Properties/Settings/Advanced/General. To check/change this setting, go to the Control Panel, choose Display properties option, then choose the Settings tab, and press the Advanced button at the right-hand corner of the tab. Changing this setting requires rebooting the operating system.

Petrolog3 can be used to perform four general types of calculations: Modeling of Crystallization, Modeling of Reverse of Crystallization, Estimating Melt Liquidus Association, and Modeling of Melt Inclusions in Olivine.

Each calculation type can be selected by choosing the appropriate tab from the main window of the software, which opens when the program is loaded. Four tabs corresponding to the four calculation types are called "Crystallisation", "Reverse Crystallisation", "Melt Liquidus Association" and "Olivine MI"

The "Modeling of Crystallization" tab is shown on Figure. 1.

Each tab window has three main parts: the top part (grey background) is used to set calculation parameters (Parameters Section); the middle part (white background) is for the output of calculation results (Output Section); and the bottom part (grey background) is for the output of non-critical debugging messages and warnings (Debug Section).

The Parameters Section has a number of boxes with white background (e.g., "Calculation step" or "Initial pressure"), in which parameter values can be typed in, and a number of settings in blue, which can be changed by clicking on them and choosing a different setting in a pop-up window.

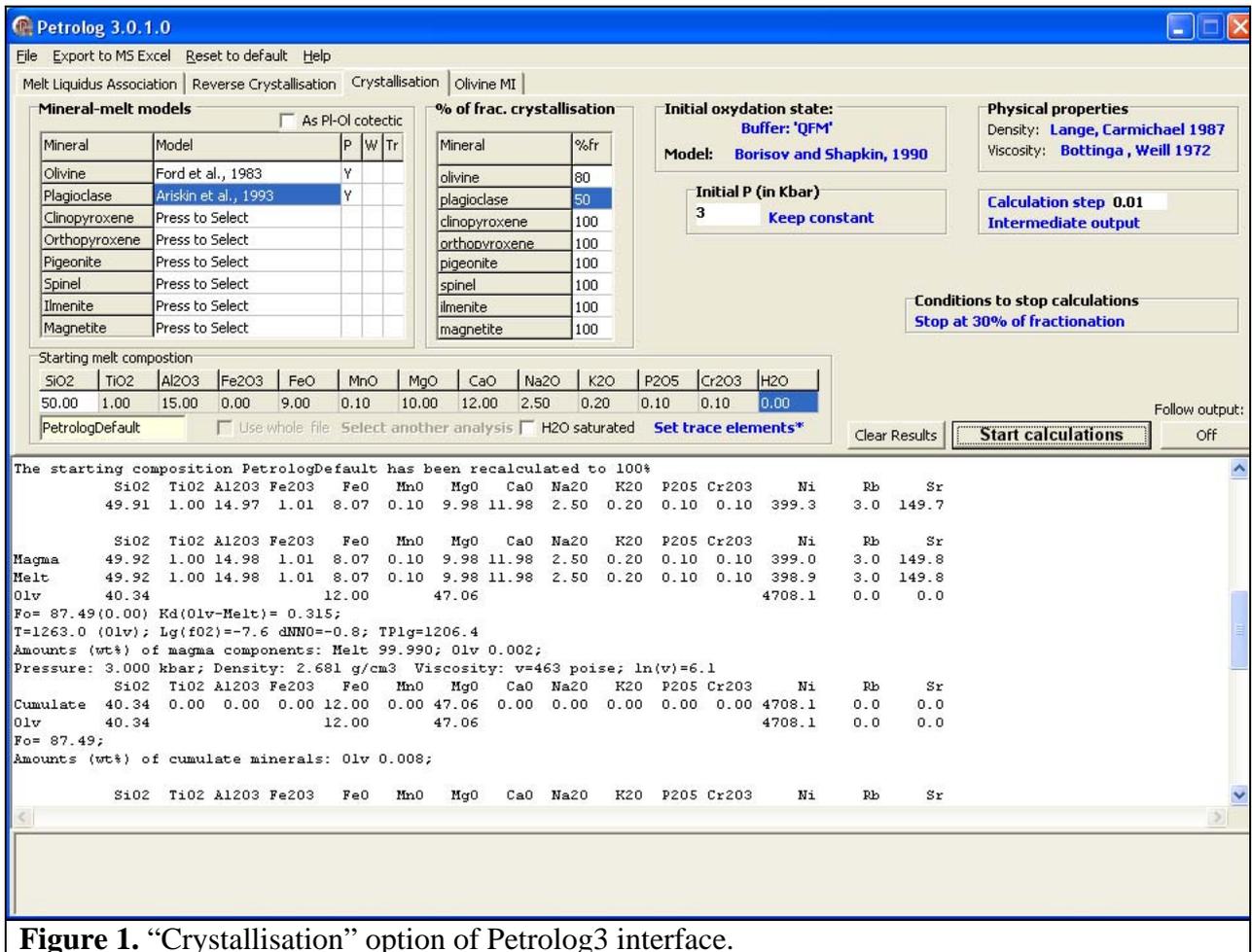


Figure 1. “Crystallisation” option of Petrolog3 interface.

When parameters are set, calculations are started by pressing the “Start Calculations” button at the right-hand corner of the Parameters Section. The Output Section will list the set of parameters chosen for calculation and calculation results. Text in the Output Section can be highlighted and copied into the Windows clipboard by pressing **Ctrl-C**, and then pasted into a text editor.

When calculation start, the “Start Calculations” button changes to the “Interrupt Calculations” button, which can be used to abort the current run.

The program is loaded with a default set of parameters and a default starting composition (PetrologDefault), and thus pressing “Start Calculations” button straight after the program is loaded would result in a default calculation.

2. Modelling of crystallisation

To model crystallization, chose “Crystallisation” tab of the Main Window (Figure 1).

2.1. Starting composition

The starting composition is set in the “Starting Melt Composition” subsection of the Parameters Section.

Petrolog3 allows the starting composition to be entered manually or loaded from a file.

2.1.1. Manual entry of the starting composition.

When the program is loaded, the “Starting melt composition” subsection of the Parameters Section contains the default starting composition PetrologDefault. This composition can be edited directly within this section. The concentrations of major elements are in wt% oxides.

Trace element contents and values for trace element distribution coefficients for each mineral are set and/or edited by clicking on ‘Set trace elements’ label, which opens the “Trace Elements” pop-up window (Fig 2).

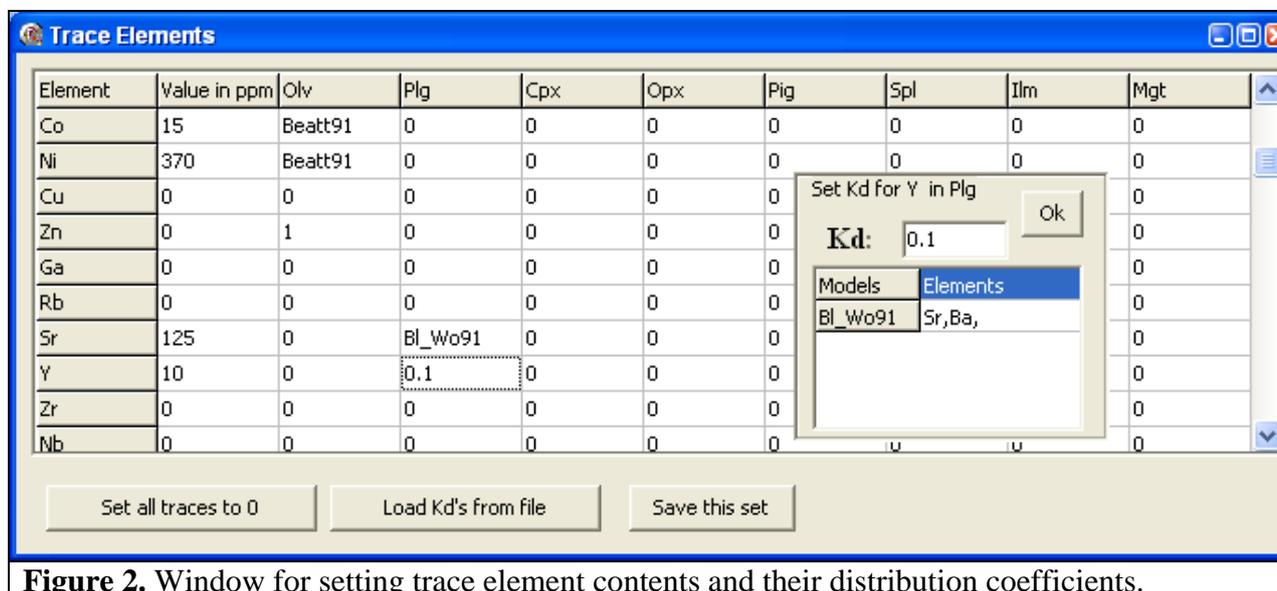


Figure 2. Window for setting trace element contents and their distribution coefficients.

The concentrations of trace elements of interest (in ppm) are entered into the first column “Value in ppm”. All elements which concentrations are not zero will be included in calculations. To reset all concentration values to zero press “Set all traces to 0” button.

Petrolog3 provides two options for defining values of distribution coefficients ($Kd_{i,min} = C_{i,min} / C_{i,melt}$, where ‘ C_i ’ is concentration in units of weight of element ‘ i ’ in mineral (min; eg, olivine, plagioclase, etc) and melt).

The first option is to set a constant Kd value, which is then used through the entire course of the calculation. To set a value, click on the cell corresponding to the element in the mineral. A pop-up window appears (Fig. 2) where Kd value can be set. All Kd values can be set without closing the pop-up window by clicking consequently on different cells of the Kd table. To close the pop-up window press “Ok” button or click on the concentration column.

The second option allows for using empirical and/or thermodynamically-sound models which define Kd values as a function of parameters, such as melt composition, temperature, mineral composition, and so on. If Kd models are available for the mineral, they will be listed in the pop-up window together with names of elements which the model applies to (Fig.2). Clicking on *the list of elements* (not the name of the model) will apply the model to all elements in the list. If required, Kd values for individual elements in the list can be later set to constant values without affecting the application of the chosen model to the remaining elements in the list.

Kd models available in the current version of Petrolog3 are Beattie et al., 1991; Kinzler et al., 1990; Blundy and Wood, 1991.

To save the chosen set of Kd values and models, press “Save this set” button. In the dialog window enter a file name *and extension, if desired*.

Note: Petrolog3 does not assign an extension to files which contain sets of Kd values.

To load a saved set of Kd values, press “Load Kd’s from file” button and chose the file name in the dialog window.

Note: To display all files on disk, choose “all files” in the “Save as file type” field. Press “Save” button to load the chosen set.

To finish editing trace element values and Kd values, close the “Trace elements” window by pressing the white-on-red cross at the top right corner.

Note: If concentrations of at least one trace element are set to a non-0 value, a star appears next to the “Set trace elements” label in the “Starting melt composition” subsection.

2.1.2. Loading starting composition(s) from file.

The starting composition(s) can also be loaded from a file by using the “Open data file” option of the File menu. The data file should contain analyses stored as rows with the first row containing element names. The program can read delimited text files, with ‘tabs’, blank spaces, and commas used as delimiters.

Note: The order of elements in the file is not prescribed. Petrolog3 identifies elements by analyzing the first row of the data file.

The following abbreviations should be used for major and trace elements (not case sensitive): SiO₂, TiO₂, Al₂O₃, Fe₂O₃, FeO, FeO*, MnO, MgO, CaO, Na₂O, K₂O, P₂O₅, Cr₂O₃, B, Be, Sc, V, Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, Re, Os, Pb, Th, U. Concentrations of major elements should be supplied in wt% oxides, for trace elements in ppm.

When a file is loaded, the first analysis in the file is displayed in the “Starting melt composition” subsection. The values in this analysis can be edited in Petrolog3 without affecting the data file on disk. When the “Start calculations” button is pressed, the calculations will start using the composition displayed in the “Starting melt composition” subsection.

Note: The starting composition in the “Starting melt composition” subsection does not change during calculations and can be used in subsequent calculations if required.

Note: When a file is loaded, its name and full path are displayed at the top of the Petrolog3 window.

If the data file contains more than one analysis, it is possible to choose another analysis by clicking on the “Select another analysis” label in the “Starting melt composition” subsection, which becomes active. In the pop-up window that appears, double-click on the analysis required. The concentration values for this analysis appear in the “Starting melt composition” subsection. To close the “Select analysis” window click on the cross at the top right corner.

2.1.2.1. Calculating multiple analyses from file.

Petrolog3 offers an option of calculating all analyses in the data file using the same set of calculation parameters. When a data file is loaded, the “Use whole file” check box becomes active, if there is more than one analysis in the file. When the “Use whole file” box is checked, Petrolog3 ignores the composition in the “Starting melt composition” subsection, and instead reads consequently analyses from the data file specified.

2.2. Setting calculation parameters

The following calculation parameters can be set before starting calculations: 1) the set of minerals involved in calculations; 2) mineral-melt equilibrium model for each mineral; 3) proportion of fractionation for each mineral; 4) pressure; 5) melt oxidation state; 6) calculation step; 7) conditions to stop calculations; 8) conditions for the output of intermediate results during calculation. These are described in detail below.

2.2.1. Choosing minerals and mineral-melt equilibrium models

Minerals and models are chosen in the “Mineral-melt models” subsection of the Parameters Section (Fig. 1).

When “press to Select” is written in the “Model” field next to a mineral name when “Start calculations” button is pressed, this mineral *will not* be included in calculations. If a model abbreviation is written next to a mineral name (e.g., Ford et al., 1983 next to Olivine on Fig. 1), the mineral *will* be included in calculations.

To choose a model for a mineral, click on the “Model” field for that mineral. A pop-up window with a list of models available for this mineral will appear (Fig. 3)

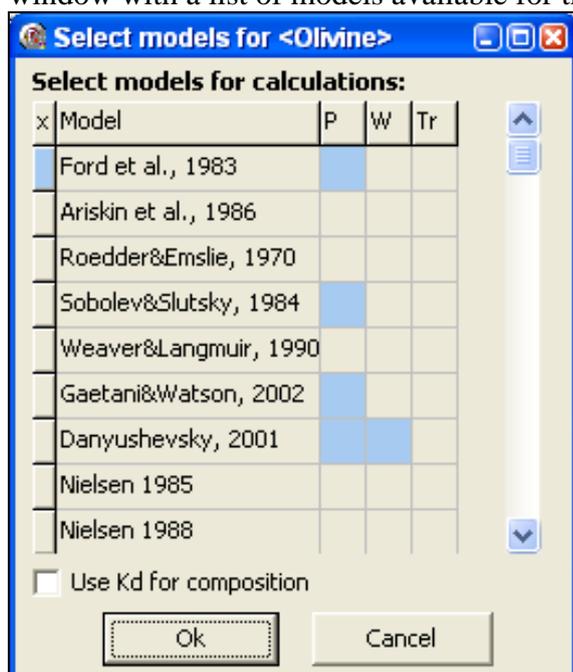


Figure 3. Window for choosing an olivine-melt model to be used in calculations.

This window is a table with 5 columns. The “Model” column lists model abbreviations.

Column ‘P’ indicates if a model incorporates the effect of pressure on mineral-melt equilibrium, or alternatively is designed for the atmospheric pressure only. If the ‘P’ cell for a model is blue, this indicates that the model incorporates pressure.

Column ‘W’ indicates if a model incorporates the effect of H₂O on mineral-melt equilibrium, or alternatively is designed for anhydrous conditions only. If the ‘W’ cell for a model is blue, this indicates that the model was developed for both anhydrous and hydrous conditions.

Column ‘TR; indicates if a model incorporates any trace elements. If the ‘TR’ cell for a model is blue, this indicates that the model incorporates some trace elements.

Blue rectangle to the left of Ford et al. (1983) model (Fig. 3) indicates that this model is currently chosen for calculations.

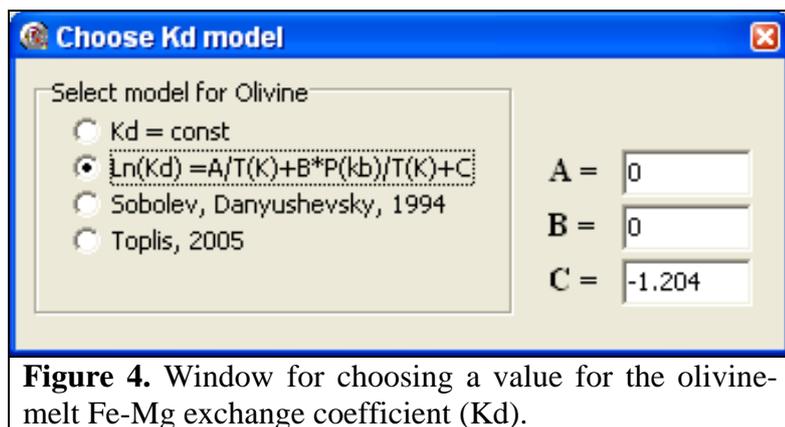


Figure 4. Window for choosing a value for the olivine-melt Fe-Mg exchange coefficient (Kd).

When choosing a model for olivine-melt equilibrium, the “Use Kd for composition” check box at the bottom of the form can be used to set an olivine-melt Fe-Mg exchange Kd value to calculate olivine composition. When the box is checked, a pop-up window appears that is used to set a Kd values (Fig. 4).

Four options are available for calculating Kd values:

- 1) **Kd=const.** If this option is chosen, a Kd value must be specified that will be used in calculations.
- 2) **$\ln(Kd) = A/T(K) + B \cdot P(kbar)/T(K) + C$.** If this option is chosen, values for coefficients **A**, **B** and **C** must be provided. The default values correspond to Kd=0.3.
- 3) **Sobolev, Danyushevsky 1994.** When this option is chosen, Kd values will be calculated following the method described in the Appendix 1 of Sobolev, Danyushevsky (1994).
- 4) **Toplis, 2005.** When this option is chosen, Kd values will be calculated using the method of Toplis (2005).

Note: When calculating olivine composition using a Kd value, the olivine-melt equilibrium model chosen in the “Select models for Olivine” window (Fig. 3) is used for calculating olivine crystallization temperature, whereas olivine composition is calculated using the specified Kd value.

To close the “Choose Kd Model” window, press the cross at the top right corner.

To deselect the Kd option, uncheck the “Use Kd for composition” box by clicking on it when it is checked.

The current version of Petrolog3 includes the following mineral-melt equilibrium models:

Olivine-melt equilibrium models: Ariskin et al., 1986; Ariskin et al., 1993; Beattie, 1993; Danyushevsky, 2001; Ford et al., 1983; Gaetani and Watson, 2002; Herzberg and O’Hara, 2002; Langmuir et al., 1992; Nielsen, 1985; Nielsen, 1988; Putirka, 2005; Roeder and Emslie, 1970; Sobolev and Slutskiy, 1984; Weaver and Langmuir, 1990.

Plagioclase-melt equilibrium models: Ariskin and Barmina, 1990; Ariskin et al., 1993; Danyushevsky, 2001; Drake, 1976; Langmuir et al., 1992; Nielsen, 1985; Nielsen and Dungan, 1983; Plechov and Gerya, 1998; Weaver and Langmuir, 1990.

Clinopyroxene-melt equilibrium models: Ariskin et al., 1986; Ariskin et al., 1993; Danyushevsky, 2001; Langmuir et al., 1992; Nielsen, 1985; Nielsen, 1988; Nielsen and Drake, 1979; Weaver and Langmuir, 1990.

Orthopyroxene-melt equilibrium models: Ariskin et al., 1993; Beattie, 1993; Bolikhovskaya et al., 1995; Nielsen and Drake, 1979.

Pigeonite-melt equilibrium models: Ariskin et al., 1986; Ariskin et al., 1993; Bolikhovskaya et al., 1995; Nielsen, 1988.

Spinel-melt equilibrium models: Ariskin and Nikolaev, 1996; Nielsen, 1985.

Ilmenite-melt equilibrium models: Ariskin and Barmina, 1999; Nielsen, 1985.

Magnetite-melt equilibrium models: Ariskin and Barmina, 1999.

2.2.1.1. Setting a pressure correction.

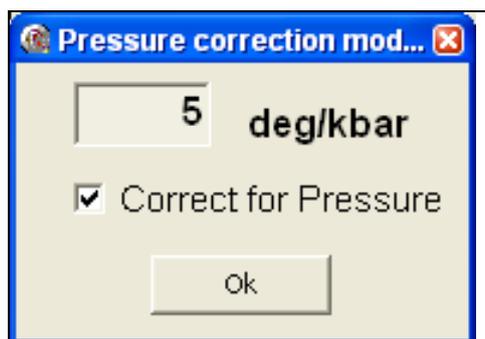


Figure 5. Window for setting a correction for the effect of pressure on liquidus temperature.

Petrolog3 offers an option to introduce a user-defined linear correction for the effect of pressure on crystallization (liquidus) temperature calculated by a model. A separate correction value can be set for of each mineral involved in calculations. To set a correction, click on the ‘P’ cell next to the chosen model. This opens a pop-up window where a correction value in degrees/kbar can be set (Fig. 5).

Note: A correction can be set to the calculated temperature regardless of whether the chosen model incorporates pressure.

Note: A correction, once chosen, applies to all models, i.e., if the mineral-melt model is changed after the correction is set, the correction will apply automatically to the new model. To remove the correction, open the “Pressure correction” window again and uncheck the “Correct for Pressure” box. If correction is set, small letter ‘c’ appears in the ‘P’ cell next (Fig. 6).

Note: Setting a user-defined correction for the effect of pressure on the liquidus temperature, does not affect the mineral composition that the chosen model calculates.

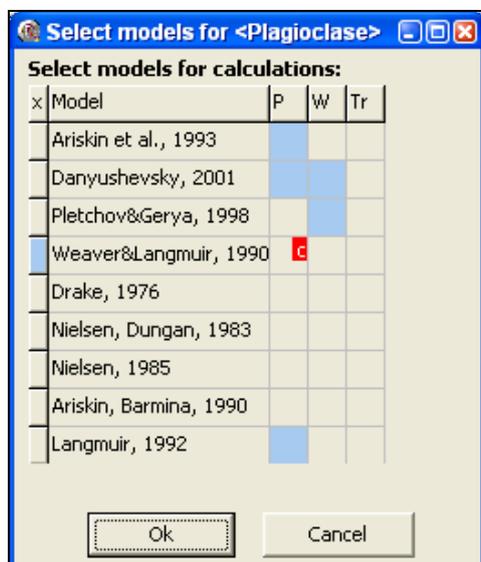


Figure 6. Window for choosing a mineral-melt model with ‘c’ in column ‘P’ next to the chosen model indicating that a pressure correction is set.

2.2.1.2. Setting an H2O correction.

As only a few models available in Petrolog3 incorporate the effect of melt H₂O content on crystallization temperature and/or composition of crystallizing minerals (Plechov and Gerya, 1998; Danyushevsky, 2001; Putirka, 2005), Petrolog3 allows the user to introduce corrections to the ‘anhydrous’ models for the effect of H₂O on crystallization temperatures, to enable calculations under hydrous conditions with models developed for anhydrous conditions only. Similarly to the pressure correction described above, such a correction does not affect the calculated mineral compositions.

To set a correction, click on the ‘W’ cell next to the chosen model. This opens a pop-up window (Fig. 7) where a correction can be set in a form $dT (^{\circ}C) = A * (H_2O \text{ wt}\%)^B$ (Falloon and Danyushevsky, 2000), which can also be used to introduce a linear correction, when B is set to 1.

Note: A correction can be set to the calculated temperature regardless of whether the chosen model incorporates H₂O.

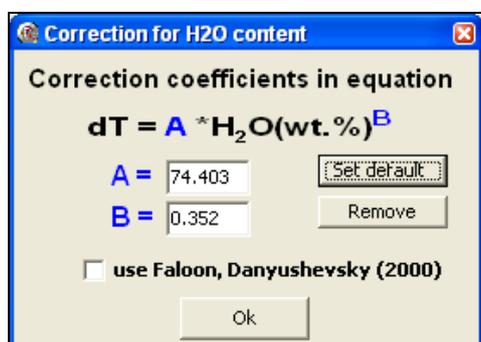


Figure 7. Window for setting a correction for the effect of H₂O on liquidus temperature.

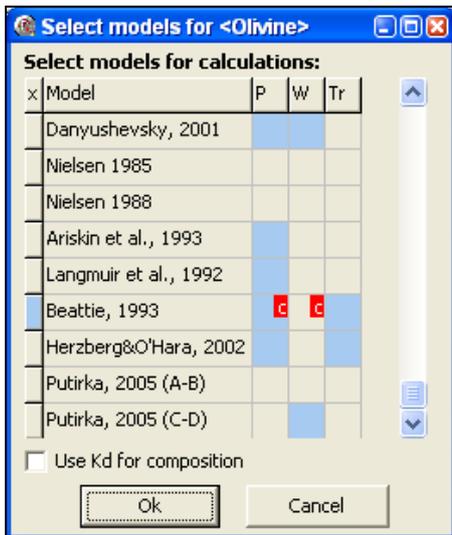


Figure 8. Window for choosing a mineral-melt model with ‘c’ in columns ‘P’ and ‘W’ next to the chosen model indicating that a pressure correction and an H₂O correction are set.

Mineral-melt models As Pl-Ol cotectic

| Mineral | Model | P | W | Tr |
|---------------|----------------------------|---|---|----|
| Olivine | Beattie, 1993 | Y | c | Y |
| Plagioclase | Weaver&Langmuir, 1990 | c | c | |
| Clinopyroxene | Danyushevsky, 2001 | Y | Y | |
| Orthopyroxene | Bolikhovskaya et al., 1996 | Y | c | |
| Pigeonite | Press to Select | | | |
| Spinel | Ariskin & Nikolaev, 1996 | c | c | |
| Ilmenite | Press to Select | | | |
| Magnetite | Ariskin, Barmina 1999 | c | c | |

Figure 9. The “Mineral-melt models” subsection of the Parameters Section showing selected mineral-melt models, whether or not they incorporate pressure, H₂O and trace elements, and which corrections are set for the effects of pressure and H₂O.

Note: A correction, once chosen, applies to all models, i.e., if the mineral-melt model is changed after the correction is set, it will apply automatically to the new model. To remove the correction, open the “Correction for H₂O content” window again and press the “Remove” button. If a correction is set, small letter ‘c’ appears in the ‘W’ cell next (Fig. 8).

The “Mineral-melt models” subsection of the Parameters Section (Fig. 1) display the models chosen for each mineral and uses columns ‘P’, ‘W’, and ‘Tr’ to indicate whether the chosen models incorporate effects of pressure and/or H₂O, and/or trace elements, and whether any user-defined correction are set for the effects of pressure and melt H₂O contents. Capital ‘Y’ is used to indicate that a model includes a corresponding effect, whereas ‘c’ is used to indicate that a correction is set (Figure 9.)

2.2.1.3. Hydrous calculations.

Petrolog3 uses the model of Moore et al. (1998) to determine the solubility of H₂O in the melt at a given T and P. When the amount of H₂O in the melt exceeds the solubility value, excess H₂O is assigned to a separate ‘fluid’ phase. Petrolog3 models degassing in a closed system, ie, it is assumed that ‘fluid’ remains within the ‘magma’. Petrolog3 also offers an option to perform the entire calculation under H₂O-saturated conditions. To use this option, check the “H₂O saturated” box within the “Starting melt composition” subsection of the Parameters section of the main form (Fig. 1).

2.2.1.4. Calculating an olivine - plagioclase ± clinopyroxene cotectic.

Petrolog3 offers an option of forcing the starting composition on an olivine-plagioclase (+/-clinopyroxene) cotectic by adjusting melt H₂O content, following the method of Danyushevsky (2001). The essence of the approach is to first calculate the amount of H₂O which is required for the starting composition to lie on an olivine-plagioclase cotectic, and then to model crystallization with this H₂O content in the starting composition, so that the composition is cotectic from the onset of crystallization. (see Danyushevsky, 2001 for a detailed description of the approach). The set of minerals is limited to olivine, plagioclase and clinopyroxene, and the set of models is limited to those from Danyushevsky (2001).

To use this option, check the “As Pl-Ol cotectic” box in the “Mineral-melt models” subsection of the Parameters Section (Fig. 9).

Note: This option should be used for MORB and BABB compositions only, as the models of Danyushevsky (2001) have not been calibrated outside this compositional range.

Note: When using this option, calculation pressure should be set at a value that insures that the melt H₂O content required is less than the saturation value (see section 2.2.3)

2.2.2. Setting the extent of fractionation for each mineral

Petrolog3 allows for a specific extent of fractionation to be set for each mineral using the “% of frac. crystallisation” subsection of the Parameters Section (Fig. 1). By default, a value of 100% is assigned to each mineral, corresponding to the case of pure fractional crystallization. When modeling pure fractional crystallization, a mineral is ‘removed’ from contact with melt and placed into the ‘cumulate’ part of the system, thus retaining its original composition.

If 0% is assigned to a mineral, this corresponds to pure equilibrium crystallization. When modeling equilibrium crystallization, the total amount of the crystallized mineral remains in equilibrium with the residual melt, thus continuously changing its composition. No ‘cumulate’ is formed during equilibrium crystallization.

When a number between 0 and 100 is entered for a mineral, this proportion of the mineral is continuously ‘removed’ from contact with the melt preserving its composition, whereas the remainders of the mineral re-equilibrates with the continuously evolving melt.

2.2.3. Setting calculation pressure

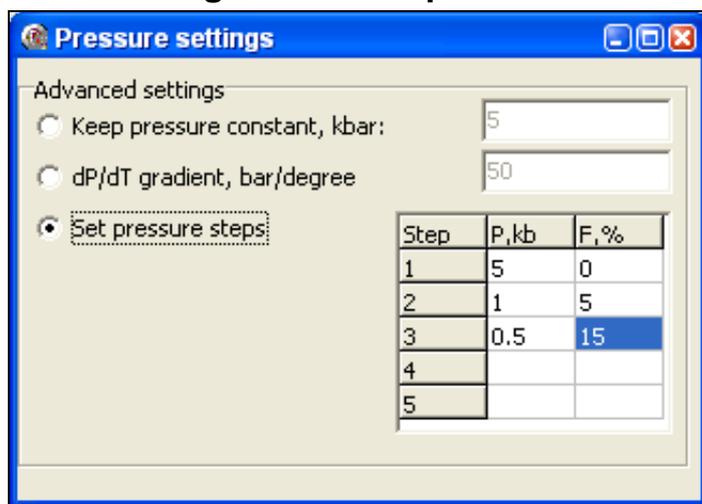


Figure 10. The “Pressure settings” window showing three available options for controlling pressure during calculations.

A value of pressure to be used during calculations is set in the “Initial P” subsection of the Parameters Section (Fig. 1). A value at the onset of calculations (in kbar) can be set in the text box within this subsection. To determine how pressure changes during calculations, click on the blue text label next to the text box in this subsection. This will open the “Pressure settings” pop-up window (Fig. 10).

By default, the “Keep pressure constant” option is chosen.

The “dP/dT gradient” option allows for pressure to be continuously changed at a fixed rate as a function of decreasing temperature. A positive value corresponds to decreasing pressure during

crystallization. If pressure reaches 1 bar before the end of the calculations, it would remain at 1 bar for the remainder of the calculations. Setting a negative value for the gradient would result in pressure increasing during the calculations.

The “Pressure steps” option allows for changing pressure during calculations as a function of the degree of fractionation. Up to four intervals with specific dP/dF values can be set. The dP/dF value for an interval is calculated from the P and F values set as the boundary conditions for this interval. The dP/dF value can equal 0 (pressure is constant) for any number of intervals. To set it to 0, the P, kb value should be the same at the start and end of the interval.

2.2.4. Setting calculation step

A value for the calculation step is set in the “Calculation step” text box in the Parameters Section (Fig. 1). The calculation step determines the amount (in wt %) by which the crystal mass increases at each step of the calculations. The smaller the calculation step is, the longer the same calculation would take. The default value is 0.01% of the amount of melt on each step. It is not recommended to increase the calculation step.

Note: The algorithm behind Petrolog3 is designed with an assumption that the output of the intermediate states of the system would occur at frequencies which are at least 2 orders of magnitude larger than the calculation step. For examples, if the calculation step is set to 0.01%, the smallest recommended output frequency is 1%.

2.2.5. Setting conditions for intermediate output

Petrolog3 offers several options for defining conditions for the output of the intermediate states of the system during calculations. The default setting is 1 wt% of crystallization. To change this setting, click on the blue text label “Intermediate output” in the Parameters Section (Fig. 1). The “Conditions for intermediate output” window would pop-up (Figure 11). Several different options can be set simultaneously and the program will display the intermediate states of the system satisfying all of the criteria selected.

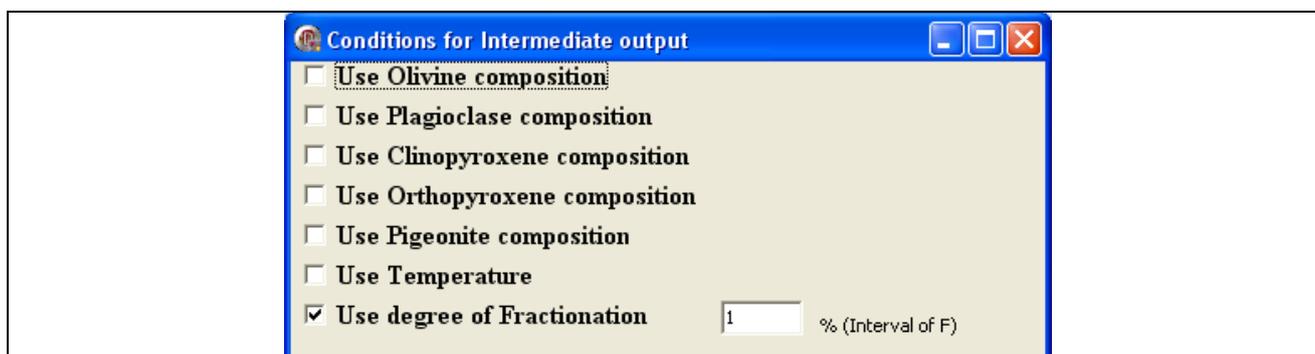


Figure 11. The “Conditions for intermediate output” window showing options available for setting conditions for the output of the intermediate states of the system during calculations.

2.2.6. Setting conditions to stop calculations

Petrolog3 offers several options for defining conditions for stopping the calculations. The default setting is 0 wt% of crystallization, indicating that no crystallization calculation is performed. To change this setting, click on the blue text label “Stop at 0% percent of fractionation” in the “Conditions to stop calculations subsection of the Parameters Section (Fig. 1). The “Conditions for stopping calculations” window would pop-up (Figure 12). Any one option can be set at a time. To close the window and save your choice, press the cross at the top right corner of the window.

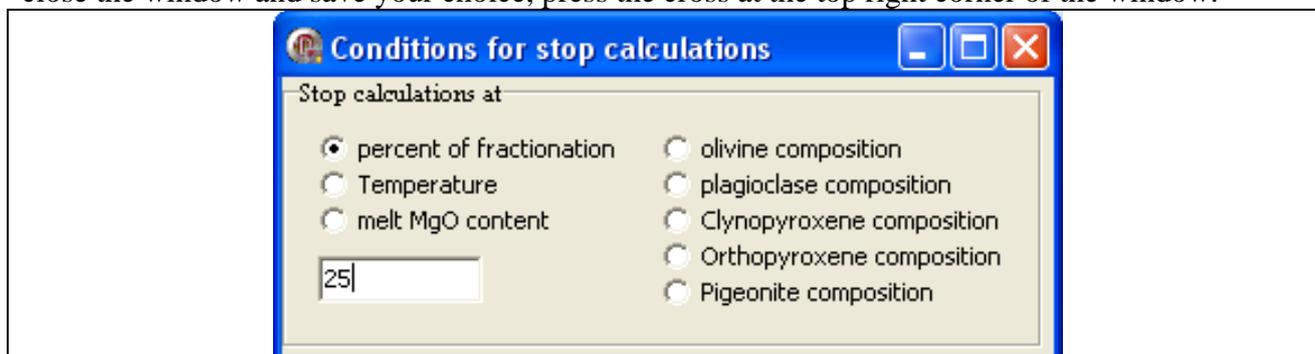


Figure 12. The “Conditions for stopping calculation” window showing options available for setting conditions for stopping calculations

2.2.7. Setting melt oxidation state

The melt oxidation state (ie, the proportion of Fe^{3+} and Fe^{2+} in the melt) during calculations is set in the “Initial oxidation state” subsection of the Parameters Section (Fig. 1): 1) calculation along an oxygen buffer; 2) calculation with a constant $\text{Fe}^{2+}/\text{Fe}^{3+}$ value; 3) calculation assuming a closed system for oxygen, and 4) defining melt oxidation state as a function of liquidus olivine composition.



Figure 13. The “Oxygen fugacity advanced options” window showing four available options for controlling melt oxidation state during calculations.

The default option is calculating along a QFM buffer of oxygen fugacity. Clicking on blue text label “Buffer: ‘QFM’” opens the “Oxygen fugacity advanced options” pop-up window (Fig. 13).

This window allows choosing one of the four options for controlling oxygen fugacity, changing the oxygen buffer used, and setting a model to calculate the melt oxidation state as a function of melt composition, temperature and oxygen fugacity.

Click on blue text label “QFM” to open the “Oxygen Buffers” pop-up window (Fig. 14).

Petrolog3 offers eight oxygen fugacity buffers. To choose a buffer click on one of the check boxes next to the buffer name. You can also specify a shift from the buffer in \log_{10} units of $f\text{O}_2$ by specifying a positive or negative value in the “Buffer shift (log units):” text box. The following oxygen buffers are available in Petrolog3:

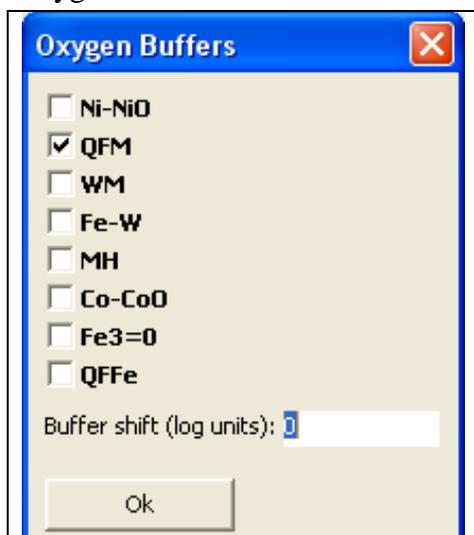


Figure 14. The “Oxygen buffers” window showing 8 available buffers of oxygen fugacity for controlling melt oxidation state during calculations.

| | |
|-----------------------|---|
| Ni-NiO | $\ln(f\text{O}_2) = -57,403.5/T(\text{K}) + 21.55;$ |
| QFM | $\ln(f\text{O}_2) = -56,280/T(\text{K}) + 19.09;$ |
| WM | $\ln(f\text{O}_2) = -85,083/T(\text{K}) + 37.04;$ |
| FeW | $\ln(f\text{O}_2) = -61,790/T(\text{K}) + 14.9;$ |
| MH | $\ln(f\text{O}_2) = -54,912/T(\text{K}) + 31.03;$ |
| Co-CoO | $\ln(f\text{O}_2) = -57,726/T(\text{K}) + 18.27;$ |
| $\text{Fe}^{3+} = 0;$ | |
| QFfe | $\ln(f\text{O}_2) = -63,362.5/T(\text{K}) + 14.73;$ |

Close this window by pressing the “Ok” button.

You need also to choose a model that defines melt oxidation state as a function of melt composition, temperature and oxygen fugacity. The default model is Borisov and Shapkin, 1990. Click on the blue text label “Borisov and Shapkin, 1990” on the “Oxygen fugacity advanced options” pop-up window (Fig. 13), to open the “Melt oxidation state model” pop-up window (Fig 15).

Choose a model by clicking on a check box next to the preferred model. The following four models are available in Petrolog3:

Sack et al., 1980; Kilinc et al., 1983; Kress and Carmichael, 1988; Borisov and Shapkin, 1990.

Alternatively, the “Melt oxidation state model” pop-up window (Fig 15) can be opened directly from “Initial oxidation state” subsection of the Parameters Section (Fig. 1).

When using an oxygen buffer to define melt oxidation state, the $\text{Fe}^{2+}/\text{Fe}^{3+}$ value in the melt will be calculated from the oxygen fugacity value corresponding to the chosen buffer, following the chosen model for the oxidation state.

When using a constant $\text{Fe}^{2+}/\text{Fe}^{3+}$ value to set melt oxidation state, oxygen fugacity is calculated from the $\text{Fe}^{2+}/\text{Fe}^{3+}$ value of the melt following the chosen model for the oxidation state (Fig. 15).



Figure 15. The “Melt oxidation state model” window showing 4 available models that define melt oxidation state as a function of melt composition, temperature and oxygen fugacity during calculations.

When calculating assuming a closed system for oxygen, the Fe_2O_3 and FeO in the starting composition are treated as ‘independent’ elements. Oxygen fugacity is calculated from the $\text{Fe}^{2+}/\text{Fe}^{3+}$ value of the melt following the chosen model for the oxidation state (Fig. 15).

If the melt oxidation state is defined as a function of liquidus olivine composition (Fig. 13), you should specify values for coefficients **A** and **B** for the equation $(\text{Fe}^{2+}/\text{Fe}^{3+})_{\text{melt}} = \mathbf{A} * \text{Fo} + \mathbf{B}$, where Fo is the proportion of forsterite in the liquidus olivine in mol%. For a detailed description of this technique, see Danyushevsky and Sobolev, 1996.

Note: This option is only available when olivine has been chosen for calculations in the “Mineral-melt models” window.

When using this option to define melt oxidation state, oxygen fugacity will be calculated from the $\text{Fe}^{2+}/\text{Fe}^{3+}$ value of the melt following the chosen model for the oxidation state (Fig. 15).

2.2.8. Choosing models to calculate melt physical properties

Petrolog3 calculates melt density and viscosity during fractionation. To choose from the available models, click on the blue text labels within the “Physical properties” subsection of the Parameters Section (Fig. 1). Clicking on the blue text next to “Density” opens the “Density Models” pop-up window (Fig. 16). Choose the desired model by pressing on one of the radio buttons next to model names: Petrolog3 offers two models for calculating melt density: Lange and Carmichael, 1997 and Nelson and Carmichael, 1979. Close the window by pressing the “Ok” button.

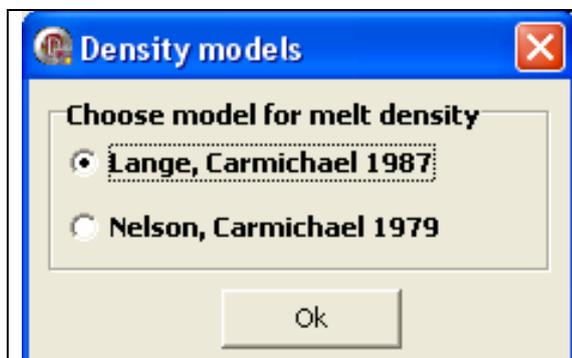


Figure 16. The “Density models” window showing two available models for calculating melt density during calculations.



Figure 17. The “Models for Viscosity” window showing two available models for calculating melt viscosity during calculations.

Clicking on the blue text next to “Viscosity” opens the “Models for Viscosity” pop-up window (Fig. 17). Choose the desired model by pressing on one of the radio buttons next to model

names. Petrolog3 offers two models for calculating melt viscosity: Bottinga and Weill, 1972 and Giordano and Dingwell, 2003. Close the window by pressing the “Ok” button.

2.3. Output of results

Petrolog3 offers three options for saving calculation results for future use.

I. During calculations, Petrolog3 prints the output into the Output Section of the Main Form (Fig.1). This output can be highlighted with the window copied (Ctrl+C) in to the clipboard to be used in a text editor.

II. Petrolog3 can save the output into a number of comma-separated values files (.csv) with a user specified name. To specify the file name, go to the File option of the Main Menu on the main form (Fig. 1) and use the “File for output...” option. A general form of the file names generated by Petrolog3 then is “UserSpecifiedName_*.csv”. The user-specified file name and its full path are displayed on the main form (Fig. 1) right above the Output Section of the Main form.

These files can either be opened manually after the calculation is finished, or can be exported into Excel by using the “Export to MS Excel” option of the Main menu on the main form (Fig. 1), and choosing the “Results of previous calculations” options. A dialog window pops-up where the user should select file “UserSpecifiedName__FRAC.csv”. This will create an Excel workbook with several worksheets containing all the details of the calculation.

Note: “FRAC” in the Petrolog3 output file names denotes files produced during calculations using the Crystallisation Option of the Main Menu (Fig. 1)

Note: Petrolog3 generates a new instance of Excel every time it exports calculation results.

Note: If the user-specified file name is not changed before the next calculation, the results of the previous calculation saved in the .csv files would be overwritten.

III. If a user specified name is not provided, Petrolog3 saves the result into a number of comma-separated values files (.csv) which names always start with “Petrolog_output_” A general form of the files name is Petrolog_output_FRAC*.csv”. These files can either be opened manually after the calculation is finished, or can be exported into Excel by using the “Export to MS Excel” option of the main menu on the main form and choosing the “Results of the last calculation” option. Since every calculation produces files with the same name, they are overridden at the beginning of calculation.

3. Melt Liquidus association

To determine melt liquidus association, choose “Melt liquidus association” tab of the Main Window (Figure 18).

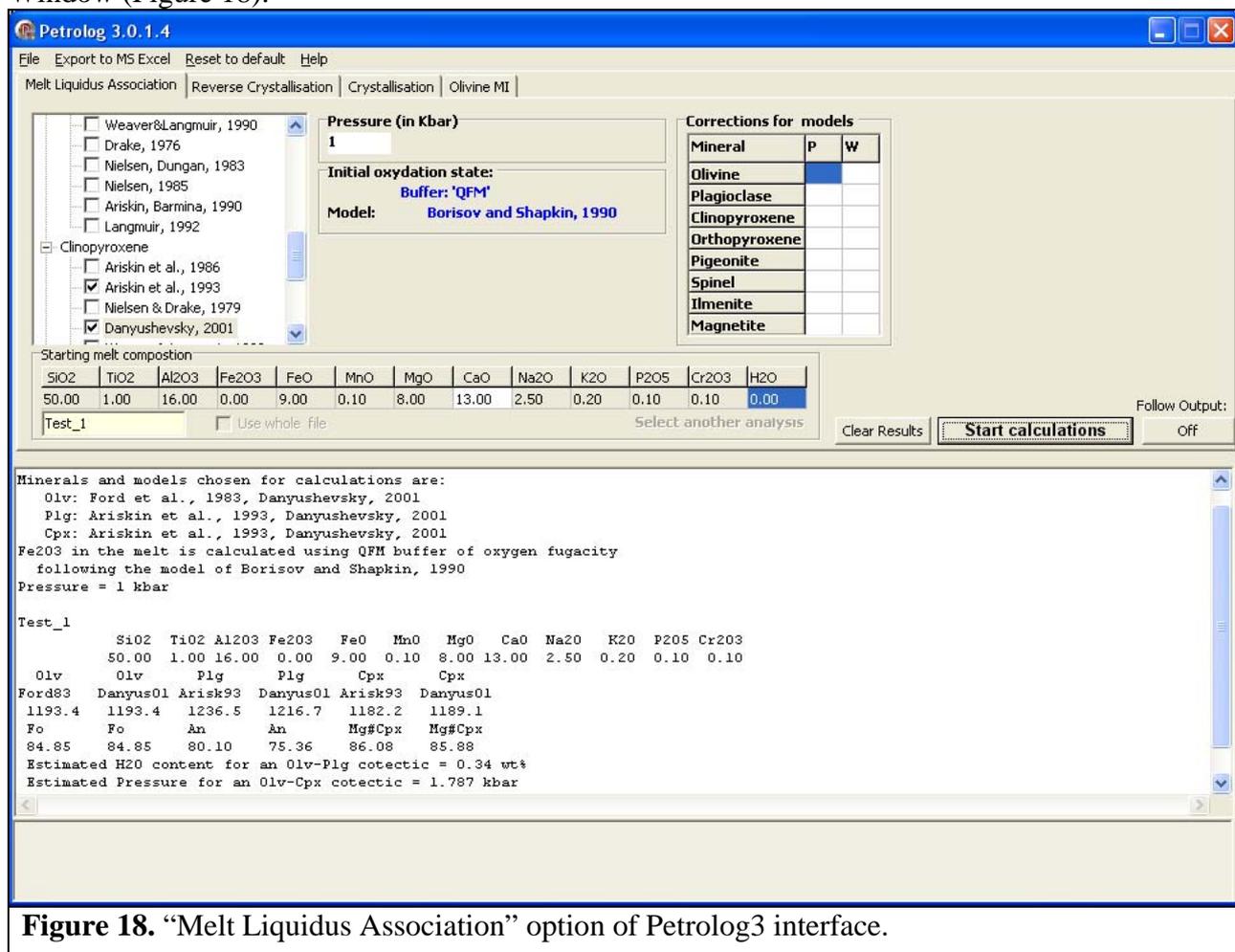


Figure 18. “Melt Liquidus Association” option of Petrolog3 interface.

Note: It is recommended that you read Section 2 of this manual before reading this section.

In this option, Petrolog3 does not model a crystallization path but calculates pseudo-liquidus temperatures and liquidus mineral compositions for a chosen set of minerals and mineral-melt equilibrium points. The following mineral compositional parameters are also calculated:

- Olivine: mol% forsterite (Fo);
- Plagioclase: mol% anorthite (An);
- Clinopyroxene; Orthopyroxene; Pigeonite; Ilmenite and Magnetite: Mg# (100*Mg/(Mg+Fe)); Cr# (100*Cr/(Cr+Al)).
- Spinel:

By comparing calculated temperatures for different minerals, the liquidus association of a melt composition can be established. As the stated errors for most models are ~ 15 - 20 °C, the liquidus association should include the mineral with the highest calculated temperature and also minerals which pseudo-liquidus temperatures are within ~ 20 °C of the calculated liquidus temperature.

Note: During melt liquidus association calculations it is possible to choose any number of models for each mineral. This allows a comparison to be made between different models.

If models of Danyushevsky (2001) for olivine AND plagioclase are chosen, Petrolog3 will automatically estimate the H₂O content in the melt which is required for this composition to lie on an olivine + plagioclase cotectic.

If models of Danyushevsky (2001) for olivine AND clinopyroxene are chosen, Petrolog3 will automatically estimate crystallization pressure at which the melt composition is saturated with both olivine and clinopyroxene.

Note: Models of Danyushevsky (2001) are calibrated for MORB and BABB compositions only.

Since crystallization calculations are not performed under this Option, the number of calculation parameters is that can be set is limited.

Handling of both the starting compositions and calculation output is the same as for the Crystallization option (See section 2.1 and 2.3 of this manual).

Note: “MLA” in the Petrolog3 output file names denotes files produced during calculations using the Melt Liquidus Association Option of the Main Menu (Fig. 18).

Corrections to the calculated liquidus temperatures for the effects of pressure and melt H₂O contents can be set in the same way as during the crystallization calculations (see sections 2.2.1.1 and 2.2.1.2 of this manual).

The melt oxidation state (ie, the proportion of Fe³⁺ and Fe²⁺ in the melt) during calculations can set in the “Initial oxidation state” subsection of the Parameters Section (Fig. 18) in the exactly the same way as during Crystallization calculations (see Section 2.2.7 of this manual).

A value of pressure to be used during calculations is set in the “Pressure (in Kbar)” subsection of the Parameters Section (Fig. 18).

4. Reverse of fractional crystallisation

To model reverse of fractional crystallization, choose “Reverse Crystallisation” tab of the Main Window (Figure 19).

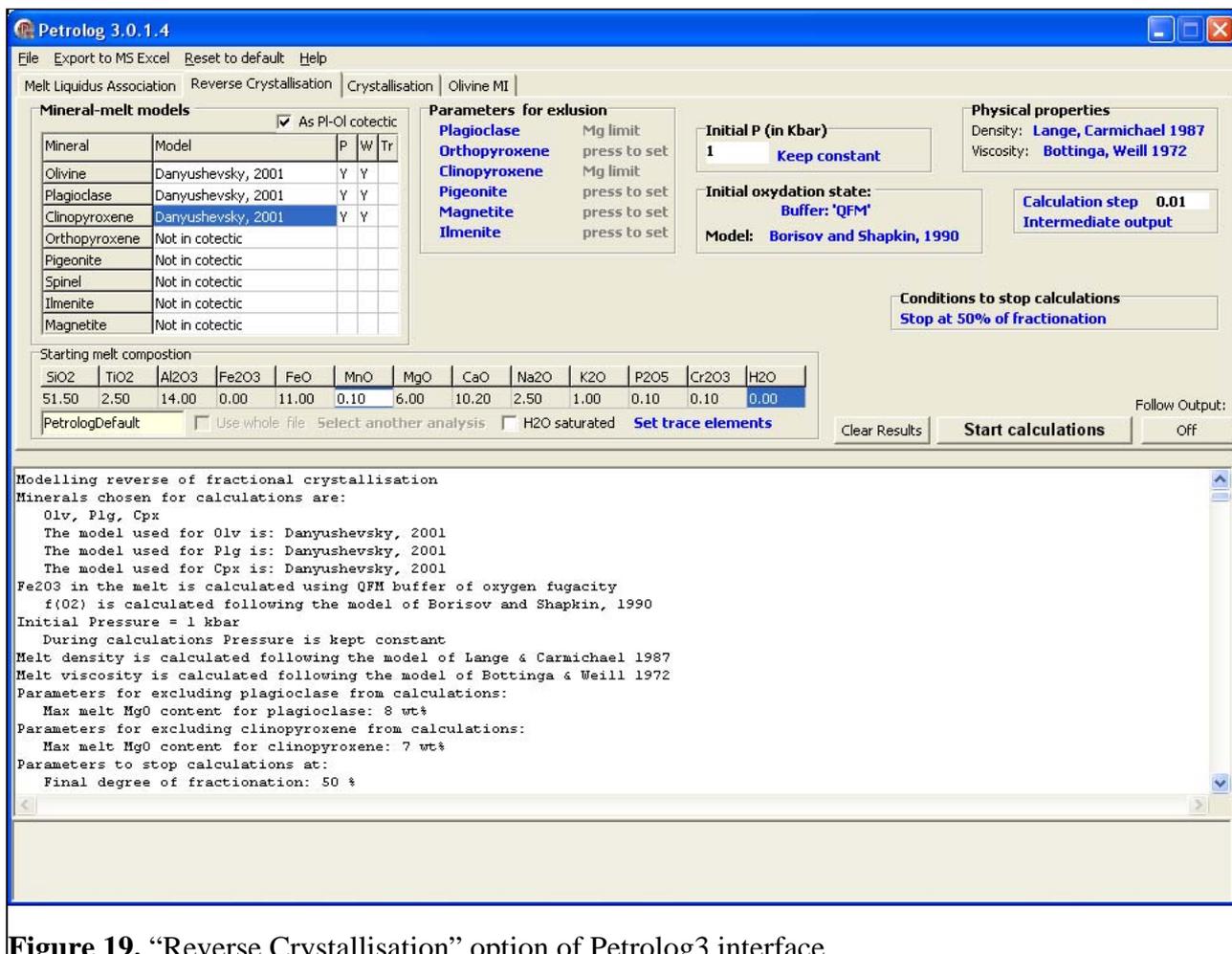


Figure 19. “Reverse Crystallisation” option of Petrolog3 interface.

Note: It is recommended that you read Sections 2 and 3 of this manual before reading this section.

The principle behind calculating the reverse of fractional crystallization is adding minerals that crystallized from the melt back to the melt composition thus moving it up along a cotectic (a liquid line of descent) towards more primitive compositions. Unlike crystallization calculations, where the mineral with the highest pseudo-liquidus temperature is subtracted from the melt composition, the mineral with the lowest pseudo-liquidus temperature is added to the melt composition during the reverse of fractionation calculations. The technique is least ambiguous when used with compositions that lie within a single phase saturation field.

Note: Fractional crystallization only can be reversed, as equilibrium crystallization does not preserve sufficient information on the crystallization history to enable reverse calculations.

Unlike crystallization calculations, when crystallization of any number of minerals can be modeled for any starting composition, with the program determining which minerals actually crystallize from the melt, the minerals that are included in the reverse of fractionation calculations *must* be on the liquidus of the starting composition at the calculation parameters chosen. Which

minerals are present on the liquidus of a starting composition can be checked using the “Melt liquidus association” option (see section 3 of this manual).

Also unlike crystallization calculations, the algorithm for modeling the reverse of fractionation does not have a built-in mechanism for determining when minerals appeared on the liquidus during fractionation, and thus these conditions should be set by the user. Consider an example with a melt composition having the following crystallization sequence: first olivine, then plagioclase after 5% crystallization (crystallization along an olivine+plagioclase cotectic), and then clinopyroxene after 15% crystallization (crystallization along an olivine+plagioclase+clinopyroxene cotectic), with a total extent of crystallization of 25%. Reversing this crystallization sequence using the evolved melt composition formed after 25% of crystallization would start with reversing crystallization along the olivine+plagioclase+clinopyroxene cotectic. However the algorithm can not determine when clinopyroxene (or plagioclase) appeared on the liquidus during fractionation, and the timing of these events should be set by the user. Thus the exact form of the calculated trend of melt evolution is dependent on the conditions at which minerals are excluded from calculations to force the trend off a cotectic.

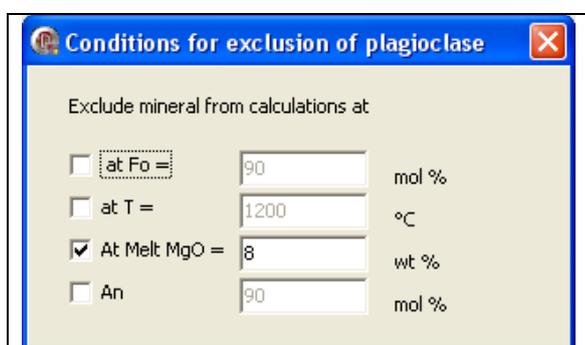


Figure 20. The “Conditions for exclusion” window, showing four available options for specifying timing of mineral exclusion from calculation.

The parameters at which the melt moves of a given cotectic (ie, parameters for mineral exclusion) are set in the “Parameters for Exclusion” subsection of the Parameters section of the main window (Figure 19). Click on the blue text label (“press to set”) next to the desired mineral to open the “Conditions for exclusion” pop-up window for this mineral (Fig. 20).

Petrolog3 offers four different options for setting the timing of mineral exclusion: 1) temperature; 2) melt MgO content; 3) composition of liquidus olivine; 4) the composition of the mineral to be excluded. Several options can be set simultaneously and the mineral will be excluded when any of the set conditions are met.

All other parameters for the reverse of fractional crystallization calculations are set in exactly the same way as for the crystallization calculation (see Section 2 of this manual).

Handling of both the starting compositions and calculation output is the same as for the Crystallisation option (See section 2.1 and 2.3 of this manual).

Note: “REV” in the Petrolog3 output file names denotes files produced during calculations using the Reverse of Fractional Crystallisation Option of the Main Menu (Fig. 19).

5. Modelling post-entrapment re-equilibration of melt inclusions in olivine

To model post-entrapment re-equilibration of melt inclusions in olivine, chose “Olivine MI” tab of the Main Window (Figure 22).

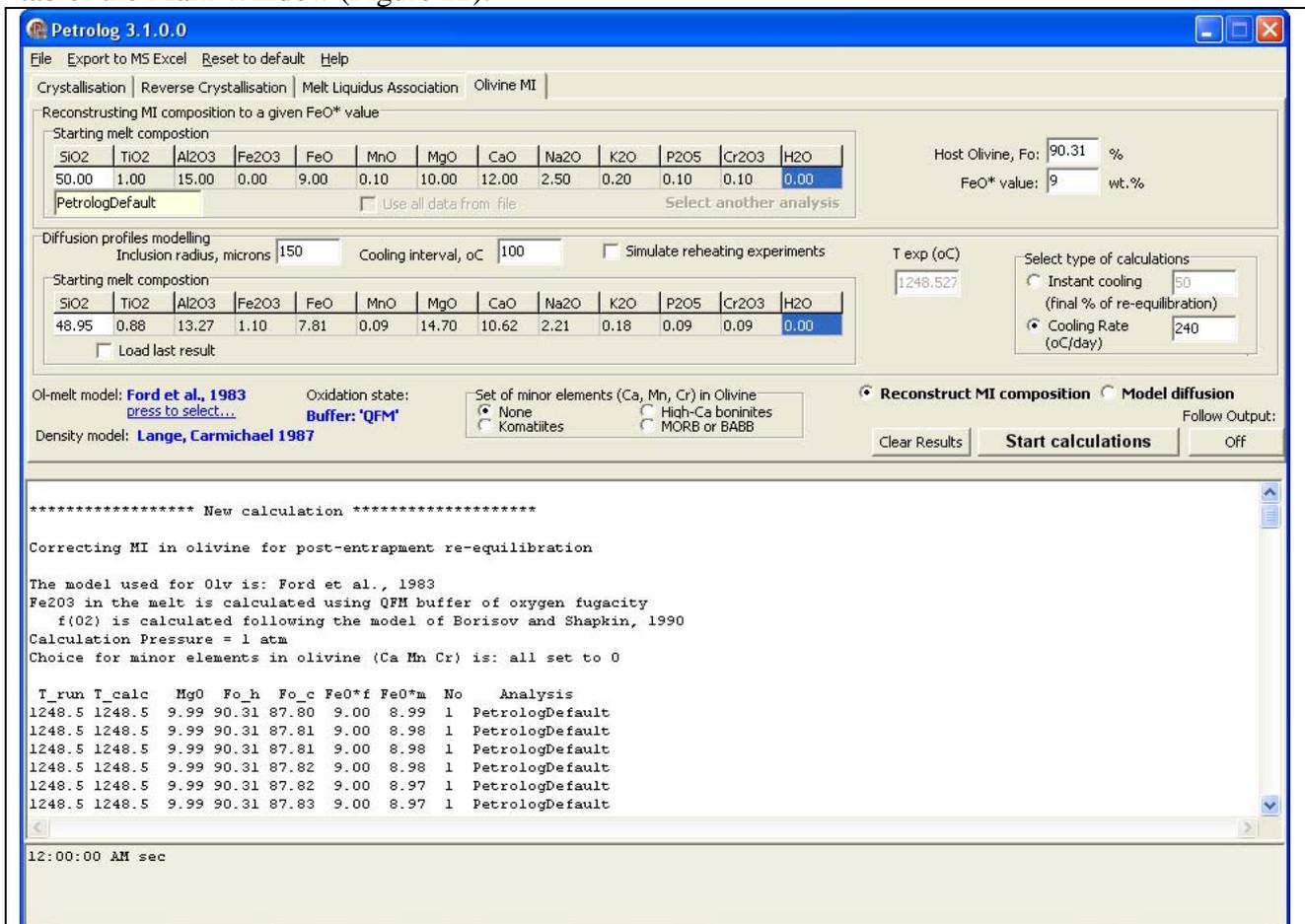


Figure 22. “Olivine MI” option of Petrolog3 interface.

Note: It is recommended that you read Sections 2, 3 and 4 of this manual before reading this section.

5.1. Reconstructing the initial trapped composition of the MI

Re-equilibration of Fe and Mg between melt inclusions and their host olivine phenocrysts is described in detail by Danyushevsky *et al.* (2000a, 2002), with the main points summarized briefly below. The underlying assumption in these considerations is that the composition of the host olivine does not change after trapping of the melt inclusion.

Cooling of an inclusion after trapping results in crystallization of olivine from the trapped melt, forming an olivine rim on the walls of the inclusion. The crystallizing olivine rim is progressively enriched in Fe and depleted in Mg, i.e., decreases in forsterite component, resulting in a compositional gradient within the rim. The existence of this compositional gradient causes re-equilibration of the inclusion with its host. This re-equilibration is achieved by diffusion of Fe out of, and Mg into the initial volume of the inclusion. This leads to a rapid decrease in Fe content of the residual melt inside the inclusion, a process referred to as “Fe-loss” by Danyushevsky *et al.* (2000a).

Conversely, if an olivine grain containing a melt inclusion is heated over the temperature of inclusion entrapment, host olivine around the inclusion would melt, increasing the Mg# of the melt inside the inclusion and resulting in disequilibrium between the melt and host olivine. This leads to

re-equilibration of the melt with the host, which is achieved by diffusion of Fe into, and Mg out of the melt inside the inclusion. This leads to a rapid increase in Fe content of the melt, a process that can be referred to as ‘Fe-gain’.

Petrolog3 offers an option of reconstructing the initially trapped melt composition, providing that the user specifies the FeO* content of the trapped melt. The algorithm simulates the following experimental procedure:

I. An olivine grain containing an inclusion is kept at a given temperature until the inclusion is in complete equilibrium with the host. Within the algorithm, this temperature corresponds to the olivine liquidus temperature of the melt inclusion composition provided (starting melt composition). The algorithm simulates exchange of Fe and Mg between melt and olivine, which occurs during the re-equilibration process. Re-equilibration may be accompanied by either melting or crystallization of the host olivine at the inclusion wall.

II. Once equilibrium is reached, the algorithm compares the FeO* content of the melt with the user-specified FeO* content of the trapped melt.

III. If the user-specified FeO* content is higher than the FeO* content of the melt, the algorithm simulates increasing experimental temperature while keeping the melt inclusion and its host in equilibrium. If the user-specified FeO* content is lower than the FeO* content of the melt, the algorithm simulates decreasing experimental temperature while keeping the melt inclusion and its host in equilibrium. In both cases this continues until the FeO* content within the melt inclusion equals the user-specified value. The algorithm simulates melting or crystallization of olivine and the exchange of Fe and Mg between melt and olivine, which occurs during this process.

To use this option, click on the “Reconstruct MI composition” radio button in the Parameters section of the main menu (Fig. 22).

The user must provide the measured composition of the melt inclusion, the composition of the host olivine (Fo, mol%), and the FeO* content of the trapped melt. These parameters are set within the “Reconstructing MI composition to a given FeO* value” part of the Parameters section of the main window (Fig. 22).

Note: Data files in this option are handled in the same way as described in section 2.1 of this manual. The host olivine composition and the FeO* content of the trapped melt must be present in the data file for each analysis, if the “calculate whole file” option is used. The column names for these two parameters should read “Fo_h” and “FeO_final, respectively (not case sensitive).

User-specified calculation parameters for this option include: olivine-melt equilibrium model; melt oxidation state, model for calculating melt density, and a model for calculating minor element contents (Ca, Mn, Cr) in olivine. The first three parameters are set in the exactly the same way as described in Section 2 of this manual.

The last parameter allows the user to introduce minor elements into the calculated olivine composition. The contents of these elements are calculated as a function of olivine Fo content, and are set to typical values for either komatiites, or high-Ca boninites, or MORB / BABB. If the contents of these elements in olivine are set to 0 (None), they are modeled as perfectly incompatible elements.

Note: All calculations within this option are performed at a pressure of 1 atm.

During calculations, Petrolog3 records intermediate output in the Output section of the main window. This output is provided mainly to keep the user informed on the progress of the calculations. Petrolog3 writes the results of calculations into a .csv file.

For each inclusion, Petrolog3 writes 3 lines into the output file. The first line, marked by value ‘1’ in the “No.” column, corresponds to the starting composition. The second line, marked by value ‘2’ in the “No.” column, corresponds to the moment when inclusion reaches equilibrium with the host (and of step I above). The third line, marked by value ‘3’ in the “No.” column, corresponds

to the final result of the calculation, when inclusion is in equilibrium with the host and the FeO* in the melt matches the user-defined value.

Note: The output files in this option are handled in the same way as described in section 2.3 of this manual. “IRL” in the Petrolog3 output file names denotes files produced during calculations using this option.

5.2. Modeling diffusive re-equilibration during ‘Fe-loss’

Known values of the diffusion coefficient for Fe-Mg inter-diffusion ($D_{\text{Fe-Mg}}$) in olivine (e.g., Chakraborty, 1997) allow calculation of the time required for re-equilibration to occur. If an inclusion is completely re-equilibrated, it is possible to calculate the minimum time that the host phenocryst spent at temperatures between trapping and diffusion closure. However, if re-equilibration is not complete when the closure temperature is reached, and thus a diffusion profile around the inclusion is preserved, a quantitative time estimate can be made.

Note: This technique does not allow an estimate of the residence time at (or close to) the trapping temperature, since at these conditions there is no (or very little) crystallization within the inclusion.

Petrolog3 offers an option for forward modeling of the re-equilibration process during cooling after entrapment (ie, for the case of ‘Fe-loss’). To choose this option, press the ‘Model diffusion’ radio button in the Parameters section of the main window (Fig. 22).

The user must provide the trapped inclusion composition, the inclusion radius (microns) and the length of the cooling interval (in °C). These parameters are set within the “Diffusion profile modeling” section of the Parameters section of the main window (Fig. 22).

Note: In this option, the starting composition cannot be imported from a data file.

User-specified calculation parameters for this option include: olivine-melt equilibrium model; melt oxidation state, model for calculating melt density, and a model for calculating minor element contents (Ca, Mn, Cr) in olivine. The first three parameters are set in the exactly the same way as described in Section 2 of this manual.

The last parameter allows the user to introduce minor elements into the calculated olivine composition. The contents of these elements are calculated as a function of olivine Fo content, and are set to typical values for either komatiites, or high-Ca boninites, or MORB / BABB. If the contents of these elements in olivine are set to 0, they are modeled as perfectly incompatible elements.

Note: All calculations within this option are performed at a pressure of 1 atm.

Diffusion modeling can be performed either for the case of instant cooling, or for the case of cooling with a specific cooling rate.

In the case of instant cooling, the zoned rim on the walls of the inclusion grows first and then re-equilibration occurs while the grain resides at the lower end of the cooling interval. To use this option, click on the “Instant cooling” radio button in the “Select type of calculations” part within the Parameters section of the main window (Fig. 22). For this option, the user needs to specify the extent of re-equilibration, a parameter that will be used to determine when diffusion calculations are completed. This parameter is set in the text box next to the “Instant cooling” radio button. The degree of re-equilibration, ie, the extent of ‘Fe-loss’, can be defined as the amount of

FeO* 'lost' by the residual melt relative to the amount that is 'lost' in the case of complete re-equilibration.

The output file generated within this option contains the melt compositions and diffusion profiles generated at different stages of calculations. The diffusion profiles are expressed as values of FeO* concentration in olivine over distance from the centre of the melt inclusion. The melt compositions recorded correspond to: 1) the starting composition, 2) the composition of the melt after instant cooling (0% re-equilibration), the composition of the melt in the case of complete re-equilibration (100%), and the composition of the melt at the required extent of re-equilibration. The FeO* profiles recorded correspond to the initial rim profile after the instant cooling, and to the resultant FeO* profile after the calculations are completed.

Note: The output files in this option are handled in the same way as described in section 2.3 of this manual. "PIC" in the Petrolog3 output file names denotes files produced during calculations using this option.

In the case of cooling with a specific cooling rate, re-equilibration and cooling occur simultaneously. To use this option, click on the "Cooling Rate" radio button in the "Select type of calculations" part within the Parameters section of the main window (Fig. 22). For this option, the user needs to specify the cooling rate, and the calculations will simulate cooling with the specified rate from the start to the end of the cooling interval. This parameter is set in the text box next to the "Cooling Rate" radio button.

Modeling of diffusion under this option is performed in 10 °C steps, with each step modeled as a separate instant cooling calculation. The program generates two output files. One file contains a record of diffusion profiles at the end of each 10-degree step, and the second file contains melt compositions at the end of each step.

Note: The output files in this option are handled in the same way as described in section 2.3 of this manual. "PCR" in the Petrolog3 output file names denotes files produced during calculations using this option. "PR" at the end of the file name denotes files containing calculated FeO profiles. "COMP" at the end of the file name denotes files containing calculated melt compositions.

To enable modeling of complex cooling histories, Petrolog3 allows for using the result of the last calculation as the starting point for the next calculation. For this purpose, after each diffusion modeling calculation Petrolog3 saves both the final profile and the final melt composition into a file called "LAST_RES.DAT". In order to use the results of the last calculation as the starting point for the following calculation, check the "Load last result" checkbox in the "Diffusion profiles modeling" part of the Parameters section of the main window (Fig. 22).

Note: Loading the results of the last calculation automatically sets the size for the inclusion radius, which should be changed.

Note: It is recommended that the user does not delete file "LAST_RES.DAT" from the directory which contains the Petrolog3 executable (ie, "Petrolog.exe" file).

Calculation under both options can simulate a reheating experiment with the melt inclusions, an optional calculation performed at the end of diffusions modeling. To include this calculation, check the "Simulate reheating experiment" checkbox within the "Diffusion profiles modeling" part of the Parameters section of the main window (Fig. 22). The user is then also required to provide a temperature value for the reheating experiment. The temperature is set in the "T exp (°C)" text box next to the "Simulate reheating experiment" checkbox.

Using this option allows Petrolog3 to reproduce the following scenario: 1) inclusion is trapped; 2) after entrapment, inclusion is cooled within the plumbing system prior to eruption; 3)

the grain with the inclusion is experimentally reheated to a certain temperature and quenched. The results of diffusion modeling can then be directly compared with the analyzed composition of the experimentally quenched inclusion.

To facilitate combining calculations of the initial trapped inclusion compositions with diffusion modeling, Petrolog3 populates the Starting melt composition for the “Diffusion profile modeling” option with the result of the calculation performed with the “Reconstructing MI composition to a given FeO* value” option. Temperature value for experimental reheating is also set to correspond to the olivine liquidus temperature of the starting composition for the “Reconstructing MI composition to a given FeO* value”.

Note: It is recommended that the user contact authors if an advanced use of the diffusion modeling is intended.

Note: If the results of a diffusion modeling calculation are intended to be used in the following calculation, simulation of the reheating experiment should not be performed.