

Niigata Perple_X Tutorial

Using this file

If you open this file in a browser the links should be enabled automatically, but in Adobe Acrobat the links are likely to be blocked. To unblock the links go to **Edit** -> **Preferences** -> **Trust Manager** -> **Internet Access from...** -> **Change settings** -> choose **Custom setting**, specify **www.perplex.ethz.ch**, and press the **Allow** button.

Getting started

If you intend to bring your personal computer, it will save time if you install Perple_X and verify your installation as described at one of the following links before the course begins:

[WINDOWS user instructions](#)

[MAC user instructions](#)

[LINUX user instructions](#)

In the above instructions, step 3 (the ability to run the programs from a console/terminal window) is worth the effort. Using Ghostview to view phase diagrams and MATLAB or PyWERAMI to view 3-dimensional data is useful, but not essential. If you have problems, feel free to contact me before the tutorial.

In addition to files mentioned above, please copy [niigata_tutorial.zip](#) and extract the files therein to your Perple_X directory.

Reading

There is no required reading for the tutorial. For reference, a few papers that describe the major aspects of Perple_X are listed at [Perple_X Citation](#). The most useful references are probably Connolly (1990, 2005, 2009) and Connolly & Galvez (2018).

The Tutorial Problem

The problem we will undertake is essentially the same as that outlined at the [Perple_X Seismic Velocity Tutorial](#) except that we will complicate the calculation by allowing redox processes and by treating the fluid as a multispecies C-O-H fluid rather than as a binary H₂O-CO₂ mixture. These complications are intended to illustrate the sorts of problems that a user normally encounters in real computations. If you already feel challenged after having installed Perple_X, then you may wish to reproduce the simpler calculation outlined at the above link.

NOTE: the tutorial has been set up so that you will need to edit the input files. Use a text editor for this purpose (e.g., Wordpad), do not use word processors such as Word, do not use tabs or special characters, and save the file as simple text.

Step 1: Run BUILD (Figure 1)

NOTE 1: if you make a mistake while running BUILD it is usually more efficient to continue and correct the mistake by manually editing **problem definition file** (e.g., **my_project.dat**) after BUILD finishes than it is to restart BUILD.

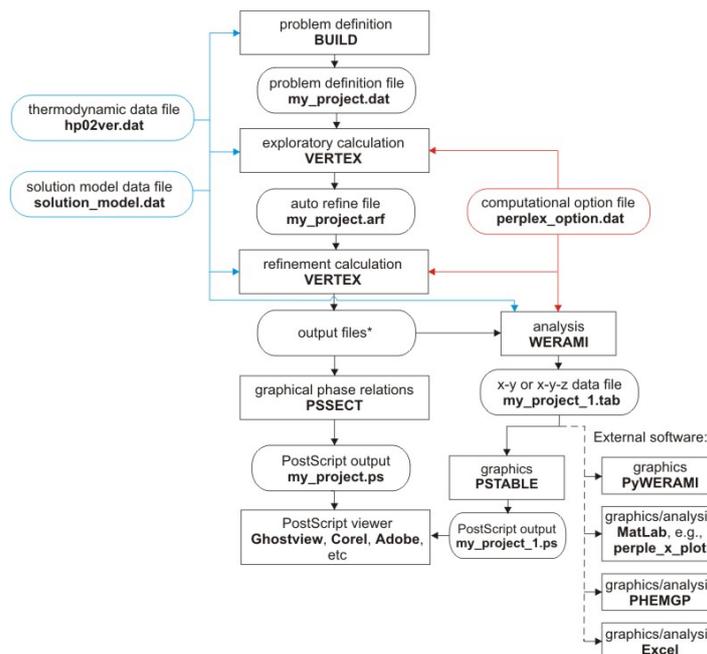


Figure 1. Program/file structure for the tutorial problem. We will use `hp02ver_niigata.dat`, `solution_model_niigata.dat`, and `perplex_option_niigata.dat` instead of the default file names indicated in the flow chart.

NOTE 2: The text of this tutorial assumes the project name **my_project**, you are free to choose whatever name you like but remember to interpret any text here that includes `my_project` as though it is your chosen project name.

Run BUILD to set up the calculation of a P - T phase diagram section for $T = 673$ - 1473 K and $P = 30$ - 80 kbar by gridded minimization for a hydrothermally altered metabasalt with composition: Na₂O 2.07; MgO 6.66; Al₂O₃ 15.53; K₂O 0.56; CaO 12.88; TiO₂ 1.10; FeO 10.02; SiO₂ 45.8; H₂O 2.68; CO₂ 2.95; O₂ 0 (amounts in wt %). By specifying O₂ as component with zero amount, we allow redox between the phases of the system, but require that the bulk composition can be described by simple oxides, i.e., that the bulk excess oxygen content relative to the simple oxide composition is zero.

Use the `hp02ver_niigata.dat` thermodynamic data file and the `perplex_option_niigata.dat` option file (the thermodynamic data file has been modified as described at [Generic Fluid EoS Models](#), explanation of the various options is at [Perple X Options](#), and details of the various thermodynamic files are at [Perple X Thermodynamic Data Files](#)).

Do not specify **saturated-** or **mobile-components**.

Exclude the following endmember phases: **h2oL** [the water endmember for the Holland & Powell (2001) melt model] and **tiGL** [the TiO₂ endmember of the Ghiorso (2004) melt model]. These endmembers are excluded because their properties are clearly anomalous. Additionally, exclude the minor fluid species **CO** and **H2**. I make this suggestion based on experience. Normally, it is best not to exclude any phases in an initial calculation and then, on the basis of that calculation, to identify and exclude anomalous or insignificant endmembers/species in subsequent refinements of the calculation.

Answer yes to the use solution models prompt. Specify the **solution_model_niigata.dat** solution model file and select the models: **Chl(HP)** [chlorite], **Mica(CF)** [white mica], **San** [alkali feldspar], **Omph(GHP)** [a model for both C2/c and P2/n clinopyroxene], **COH-Fluid** [fluid, or use the high resolution equivalent **COH-Fluid+** if you are curious about the CO and H₂ species concentrations, in this case do not exclude H₂ and CO, **COH-Fluid+** will substantially slow your calculations], **T** [talc], **Do(HP)** [dolomite], **M(HP)** [magnesite], and **Gt(HP)** [garnet]. Probably the best way to find information on the solution models is to read the commentary in the solution model file, in some cases, the [Solution Model](#) web page is also of use, though it tends to be woefully out-of-date.

Step 2: Run MEEMUM

MEEMUM is an interactive Gibbs energy minimization program that reads the same files as VERTEX. It is useful for testing and, because it does not rely on interpolation, resolving ambiguities that may arise through gridded minimization in VERTEX.

Run MEEMUM, answer no to all prompts until prompted physical conditions, enter $T = 1000$ K and $P = 30000$ bar. If the stable assemblage is Mica + Do + Gt + Cpx + F + coe + ru, you have configured the problem correctly, otherwise ask for help.

Step 3: Run VERTEX

VERTEX is the phase diagram calculator.

Run VERTEX. The **auto_refine** option in `perplex_option_niigata.dat` has been set to **off** so that VERTEX will terminate after the low resolution exploratory stage. At this point, if you are curious about what the low resolution results look like you can run PSSECT to create a PostScript file **my_project.ps**. This file can be viewed in any PostScript interpreter (Ghostview, Acrobat, Corel, etc.).

Open **my_project_auto_refine.txt** and look for an instance of **warning ver993**. In this case, the warning indicates that the composition of Mica(CF) has reached an unnatural limit imposed in the solution model (unnatural limits are often imposed in complex solution models to save time and/or memory). VERTEX automatically relaxes such limits, but they may nonetheless affect final results, therefore it is wise to eliminate any instances of this warning after the exploratory stage (`my_project_auto_refine.txt` summarizes the exploratory stage warnings, regardless of the **auto_refine** option value).

Open **solution_model_niigata.dat**, locate the Mica(CF) model, and modify the subdivision ranges of the **cel** and **fcel** endmembers so that they include the values indicated the `my_project_auto_refine.txt`.

Open **perplex_option_niigata.dat**, locate the **auto_refine** keyword and change its value from **off** to **default** (or **auto**).

Save and close the edited files. Run VERTEX again. You may wish to verify that warning ver993 is no longer present in **my_project_auto_refine.txt**.

Step 4: Run PSSECT

PSSECT plots phase diagram sections.

Run PSSECT to create a PostScript file **my_project.ps**. This file can be viewed in any PostScript interpreter (Ghostview, Acrobat, Corel, etc.). At what conditions is the metabasalt completely dehydrated? To answer this question graphically, run PSSECT again, answer **yes** to the **Modify the default plot** prompt, answer **no** to the **Modify drafting** prompt, answer **yes** to the **Restrict phase**

fields by phase identities and instruct the program to plot only phase fields including **Mica(CH)**, i.e., the most stable hydroxylated phase in the calculation.

If you wish to improve the quality of your results increase the **reach_increment** value specified for **COH-Fluid** in **solution_model_niigata.dat** from **0** to **6** and/or change **x/y_nodes** in **perplex_option_niigata.dat** from default to **40 60**.

NOTE: because the **solution_names** option in **perplex_option_niigata.dat** has been set to **abb** (abbreviation) both WERAMI and PSSECT generate output in which the solution model names have been replaced by the abbreviation keyword in the text of the solution model. E.g., stable phases of the solution model **Omph(GHP)** are identified as **Cpx**. These abbreviations cannot be used as input in **Perple_X**, i.e., input must be specified the solution model name. To generate output with solution model names set **solution_names** to **default** (or **mod**).

Step 5: Run WERAMI, the dubious consequences of allowing redox

WERAMI extracts data from calculations made with VERTEX. In operational mode 1 (properties at specified conditions) it is essentially equivalent to MEEMUM.

Run WERAMI, choose operational mode 1, specify $T = 850$ K and $P = 45000$ bar. What is the significance of the presence of two phases identified as **Cpx**? What is the ferric/ferrous ratio in these phases? What is the speciation of the C-O-H fluid (**F**)? What reaction explains the formation of this fluid?

Although the presence of the methane-rich fluid is a thermodynamically correct result, it is an artificial consequence of allowing redox processes in combination with our incorrect assumption that bulk composition can be described by simple oxides (for more discussion see Example 1 of [Generic Hybrid Fluid EoS](#)). Had we not allowed redox processes by adding O_2 as a component, we would have obtained an arguably more realistic devolatilization model at the expense of a less realistic model for mineral compositions. If anything, this result illustrates the dangers of attempting to model complex behavior in the face of imperfect knowledge. While there is no completely satisfactory solution to the problem here, the unrealistic prediction of a methane-rich fluid can be eliminated by adding excess oxygen to the bulk composition. If you are bored or running out of time, skip to Step 6, otherwise:

To compute the amount of excess oxygen, quit operational mode 1 by entering **99 99**, select operational mode 2 (**properties on a 2d grid**), choose property 6 (**composition of the system**), select the **O2** component, and answer **no** to the **Include fluid...** prompt. If you wish at this point, you may select additional properties; e.g., to plot the amount and CH_4 -content (see [Solution Composition Variables](#) for explanation) of the fluid choose properties 7 and 8, respectively (this will demonstrate that the amount of methane-rich fluid is insignificant). Terminate property selection by entering **0**, and press **<enter>** in response to the remaining prompts. WERAMI issues a warning concerning a cosmetic detail that can be safely corrected in this case, if desired, by setting the **warning_ver637** option. Once WERAMI completes the calculation it summarizes the result by indicating the maximum excess O_2 -content in the solid aggregate is 0.06 wt % and indicates that it has written the data to the file **my_project_1.tab**. To [visualize the data](#) in this file run either PSTAB, PyWERAMI, or start MATLAB and after changing directories to your **Perple_X** directory, run **perple_x_simple_plot** (the latter is the most flexible option, PSTAB generates a file that must be viewed in your PostScript interpreter).

To eliminate the predicted methane-rich fluid, open **my_project.dat** and increase the bulk O₂ content from zero to 0.06 wt % (although the units here can be interpreted as weight fractions, the input is actually extensive, thus the number 0.06 is really the mass of O₂ in grams).

Save and close **my_project.dat**. Run VERTEX and PSSECT again. Locate the conditions for the onset of devolatilization by plotting the stability field of **COH-Fluid**. Verify that the fluid composition at the onset of dehydration is no longer methane-rich with WERAMI (**mode 1**). Comparing the computed phase relations to those of the [Perple X Seismic Velocity Tutorial](#) shows unsurprisingly, at least in hindsight, that the effect of incorporating redox is insignificant unless your intention is to model the unknown ferric iron content of Cpx.

Step 6: WERAMI, using mineral compositions for thermobarometry

To illustrate the use of WERAMI for thermobarometry find the conditions at which mica [**Mica(CF)**] with a molar phengite-content (= Mg + Fe) of **0.94±0.02** coexists with garnet [**Gt(HP)**] with a grossular-content of **0.41±0.02**. The easiest way to do this is to use WERAMI (**computational mode 2**) to tabulate the composition of garnet (C_Gt = **1 gr**, gr is the grossular endmember, see [Solution Composition Variables](#) for explanation) and mica (C_Mica = **1 cel + 1 fcel**, cel and fcel are the Mg- and Fe-phengite endmembers). Then make contour plots (with PSTAB, MATLAB, or PyWERAMI) of the mica and garnet compositions, setting the lower and upper contour limits to match the range of compositions of interest and the contour interval to **0.02**, and overlay the two results. In MATLAB both contour plots can be superimposed [interactively](#) if you use the `perple_x_simple_plot` script and type **hold on** after making the first plot.

Step 7: WERAMI, mineral modes along a geotherm

In general, if you are interested in properties along a geotherm or other types of 1-dimensional paths it is more accurate to do a 1-dimensional calculation in VERTEX. However, this example demonstrates how a 2-dimensional gridded minimization calculation can be sampled along a geotherm path with WERAMI.

To improve the appearance of the plot open **perplex_option_niigata.dat**, change the values of the **fancy_cumulative_modes** and **warning_ver637** keywords to keyword to **T** and **F**, respectively.

Select WERAMI operational mode 3 (properties along a 1d path), construct a non-linear profile with temperature as the independent variable. Specify the geotherm with the polynomial $P(\text{bar}) = 25144 - 22.4 T + 0.044 T^2$ (fit for $T = 673\text{--}1400$ K), i.e., $n = 2$, $c(0) = 25144$, $c(1) = -22.4$, $c(2) = 0.044$. Specify 400 points, it does not make sense to specify much higher resolution than the computational grid used by VERTEX (313 x 313 nodes by [default](#)). Choose property 25 (modes of all phases), use cumulative modes, and include fluid in the computation. Cumulative modal plots have the advantage that the curves do not cross each other and are thus useful for systems with complex mineralogy (arguably this is not the case here). The disadvantage of using the cumulative mode plotting options is that neither PSVDRAW, PSTABLE, nor MATLAB/perple_x_simple_plot does a good job of labelling the phase fields (PSVDRAW may do the best job, but MATLAB allows interactive editing), in that respect it is useful to use WERAMI (operational mode 1) to work out which phase is stable in which field.

If you have the time and interest, plot the fluid speciation along the geotherm. If you are interested in the abundance of minor species a logarithmic plot is useful. In MATLAB you can switch between a logarithmic and linear plot by selecting the plot axes and then opening the property editor. In PSTAB you are offered the possibility of plotting values or the log of the values.

Additional/Alternative Exercises:

Open system devolatilization (phase fractionation)

Open **perplex_option_niigata.dat**: 1) Change the **absolute** keyword value to T, this will cause WERAMI to output absolute amounts (since the mass amount specified by the initial composition is ~100 g, the “absolute” amounts are actually relative to this mass). 2) Change the **1d_path** keyword value to **40 400**, this will make the grid resolution comparable to that in the previous problem.

For the system configuration outlined above in **Step 1** :

Run BUILD to set up a phase fractionation calculation (computational mode 5) to evaluate the amount and composition of the fluid that evolves during subduction along a geotherm defined by the polynomial: $P(\text{bar}) = 25144 - 22.4 T + 0.044 T^2$. Duplicate the problem definition file giving it a new name so that you have two projects, e.g., **my_project_closed** and **my_project_open**. Run VERTEX with **my_project_closed**, choose computational mode 0 (no fractionation). Plot the result using PSSECT, if everything is correct the depicted phase relations should correspond to the phase relations depicted in Step 7 above. Run WERAMI, **computational mode 3**, choose property 36 (**all phase &/or system properties**), choose **properties of a phase** and specify **COH-Fluid**. Plot the amount of H₂O, CO₂, and O₂ in the fluid as a function of temperature using PSTABLE of MATLAB. The amounts may decrease with increasing temperature (and pressure) because in the closed system model fluid may be consumed by carbonation/hydration reactions. Return to WERAMI, computational mode 3, choose property 8 (**composition of a solution**), repeat this choice three times to extract the mole fractions of H₂O, CO₂, and CH₄ in the fluid along the geotherm. Plot the species abundances.

Open **perplex_option_niigata.dat** change the **cumulative** option keyword, this will cause WERAMI to compute the cumulative amounts of the components fractionated from the system by the fluid. Run VERTEX with **my_project_open**, choose computational mode 1 (**fractionate specified phases**) and specify **COH-Fluid**. Repeat the analysis as made above for **my_project_open**. The phase relations are somewhat more complex because fluid is only stable intermittently. If you use MATLAB for plotting, edit `perple_x_simple_plot` and change the text **Marker = 'none'** to **Marker = 'o'** for clearer plots. Compare the amount and composition of the fluid in the open and closed system models.

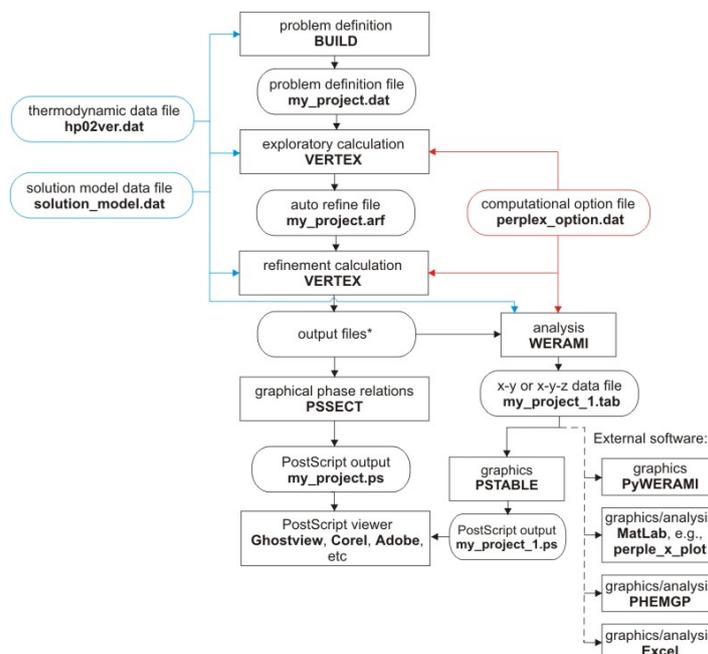


Figure 2 Program/file structure for Convexhull optimization calculations (Solution model exercises 1-3).

Solution model exercises

Solution models consist of three basic components, a mechanical mixture component, an excess component, and a configurational entropy component (see [chapters 8, 11, and 12 of my thermodynamics course lecture notes](#) for clarification of my jargon). If you are curious about how these are input into Perple_X, the following exercises may be of interest:

Exercise 1: Open the **feldspar_solution_model_exercise.dat** file. Use the site occupancy table in the comments at the beginning of the **feldspar** model to complete the site fraction expressions for $z(\text{Na})$, $z(\text{Ca})$ and $z(\text{Al})$. If the format is unclear refer to the file **solution_model_type_2_(simple)_template.dat** for more information. Once you have completed the site fraction expressions run **CONVEX** (Figure 2) with the project name **feldspar_exercise** to check your results. Once CONVEX terminates without an error, generate a PostScript plot of the results with **PSVDRAW**. To view the pseudocompounds used by CONVEX when you make a plot with PSVDRAW, you must answer yes to the **modify the default plot** prompt and then instruct the program to **draw all tielines**.

Exercise 2: This exercise is a slightly more elaborate version of the previous. Open the **biotite_solution_model_exercise.dat** file and enter the missing site fraction expressions. Run CONVEX and PSVDRAW with the **biotite_exercise** project as in Exercise 1 to check and evaluate your result.

Exercise 3: Create a solution model for Mg-Fe-Ca garnet (py-alm-gr) named **Gt(HP)** in the solution model file **garnet_solution_model_exercise.dat**, the excess function for this model should be $G_{\text{excess}} = W_{\text{py-gr}} y_{\text{py}} y_{\text{gr}}$ (with $W_{\text{py-gr}} = 33000 \text{ J/mol}$). It may be helpful to copy the model the "T" (talca) solution model from the end of **solution_model_type_2_(simple)_template.dat** and use this as a template for the garnet model. Run CONVEX and PSVDRAW with the **garnet_exercise** project as in Exercise 1 to check and evaluate your result. Does it make sense? Modify the temperatures specified at the end of **garnet_exercise.dat** to constrain the critical temperature of the garnet solvus.

If you wish to test your facility with BUILD and VERTEX, try setting up the same calculations done above as 2-d gridded minimization problems. You must define the compositional variables such that the $X(\text{C1})$ -

X(C2) compositional coordinates [0,0], [0,1], and [1,0] correspond to endmember compositions of the solution in question. In the feldspar and garnet cases there are three avenues of approach:

- 1) Specify SiO_2 and Al_2O_3 as saturated components so that remaining thermodynamic components are identical to the projected endmember compositions (e.g., after “projection” through SiO_2 and Al_2O_3 ; the composition of pyrope is MgO, etc.)
- 2) Transform the data base components using **CTANSF** so that the data base components correspond to the endmember compositions (e.g., transform MgO to $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ etc.)
- 3) Retain the original oxide components and do not saturate. The disadvantage of this approach is the composition of the solution model is degenerate in the full compositional space and small round-off errors may cause stability of additional phases (e.g., quartz or corundum).

Biotite has a more complex solution space and therefore the result in exercise 2 can only be reproduced by using method 1 above. You will need to exclude some endmember phases to prevent them from interfering with the partially metastable feldspar and Gt(HP) intra-phase relations obtained in exercises 1 and 3.

[The tutorial by Danielle Castelli and Chiara Groppo](#) (Torino) is a comprehensive collection of petrological applications

[The tutorial by Craig Bina](#) (Northwestern) outlines several geophysical applications

[The Lausanne 2016 workshop](#) outlines several metacarbonate problems

[The electrolyte page](#) provides links to files for several applications involving electrolytic fluids

The [FRAC2D](#) and [TITRATE](#) pages provide links to files for equilibrium reactive transport

[The documentation page](#) provides links to additional sources