IISc 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

Copy Perple_**X** and verify that your copy works 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 or Ghostscript 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 iisc_perple_x_tutorial.zip and extract the files in the data_files directory 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 course description and this script are included in the iisc_perple_x_tutorial.zip file archive.

The Tutorial Problem(s)

The problem we will undertake is to model the metamorphic evolution of a metabasaltic system at conditions pertinent to subduction zones. The problem is essentially that outlined at the, somewhat out-of-date Perple_X_Seismic_Velocity Tutorial except that we will complicate by treating the fluid as a binary H_2O-CO_2 mixture. If you are interested in details specific to wavespeed calculations refer to the Perple_X_Seismic_Velocity Tutorial.

Yet another alternative to the present outlined here is given the HUJI_tutorial. The HUJI_tutorial is a more elaborate variant of the IISC tutorial that treats both redox processes and electrolytic fluids. You are welcome to do the HUJI tutorial instead of the IISc tutorial, however be warned that it is more time-consuming. To do the HUJI tutorial copy the requisite files from huji_perple_x_tutorial.zip.

NOTE 1: To use Perple_**X** effectively it is important that you run the programs from a console (aka shell, terminal, or command window). Clicking on the program icons is a bad way to run the programs because it is likely you will miss error and warning messages. If you haven't yet set up a

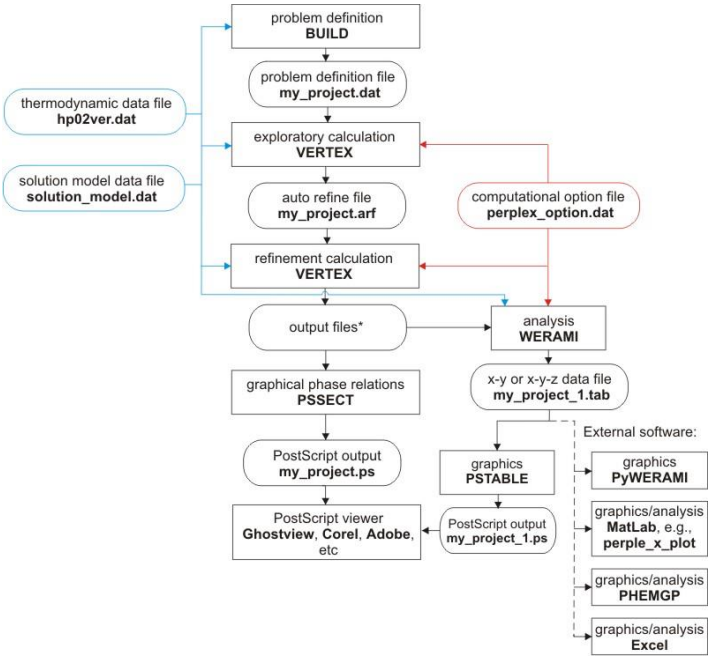

Figure 1. Program/file structure for the tutorial calculation with VERTEX.

console window, now is the time to do so (see Step 3 of the WINDOWS, MAC, or LINUX setup instructions).

NOTE 2: 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.

NOTE 3: 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.

NOTE 4: The text of this tutorial assumes the project name **my_project**, you are free to choose whatever name you like but remember to interpret text here that includes my_project as though it is your chosen project name.

NOTE 5: Computer file names usually consist of two parts as in **my_project.dat,** the first part, my_project, is referred to as the root or file-name and the second part, dat, is referred to as the file-type. By default most modern OS file viewing programs hide file-types. This can be extremely confusing, if your file viewing program does not show file-types I recommend you modify its settings.

Step 1: Run BUILD

Run BUILD (Figure 1) 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 the molar composition: Na_2O 0.328; MgO 1.623; Al_2O_3 1.497; K_2O 0.058; CaO 2.258; TiO_2 0.138; FeO 1.370; SiO_2 7.490; H_2O 1.460; CO_2 0.659.

Use the **HP02ver.dat** thermodynamic data file and the **perplex_option.dat** option file.

Do not specify a **saturated fluid phase**.

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

Answer yes to the **print file** prompt.

Answer yes to the **exclude endmembers** prompt and exclude the **h2oL**, **TigL**, and **tan** endmembers. In general, it is best practice to **not** exclude any endmembers/species in an initial calculation. Once this calculation has been inspected features associated with bad or incompatible can be corrected by exclusions. Exclusions must be justified, by that I mean that you should not exclude things simply because you do not like them, e.g., you should not exclude quartz because you only see coesite in the rocks you are interested in. Here **h2oL**, the water endmember for THERMOCALC melt models, and **TigL**, the titanium endmember for Mark Ghirso's PMELTS model are excluded because their high-pressure, low-temperature, properties are incorrect and result in the prediction of a low-temperature melt field. This endmember cannot be excluded from super-solidus calculations. In such cases, the calculation can be split into low- and high-temperature sections or the T_melt option can be set to destabilize the endmember at low temperature. And **tan** is a hypothetical talc endmember that is meant for a talc solution model that is not used here.

Answer yes to the use **solution models prompt**. Specify the **solution_model.dat** solution model file and select the models: **Bio(TCC)** [biotite], **Mica(CF)** [white mica], **feldspar** [ternary feldspar, a model for plagioclase and orthoclase], **Omph(GHP)** [a model for both C2/c and P2/n clinopyroxene], **COH-Fluid** [fluid], **T** [talc], **Do(HP)** [dolomite], **M(HP)** [magnesite], and **Gt(HP)** [garnet]. 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.

BUILD writes the problem definition file to **my_project.dat**. This file can be edited to avoid the tedium of running BUILD every time you want to modify the configuration of a problem.

Step 2: Run MEEMUM

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

i) Edit the option file (**perplex_option.dat**): change the value of **solution_names** from **default** to **abb**; save your edits.

ii) Run MEEMUM, answer no (or simply press enter) to all prompts until prompted for physical conditions, enter T = 673 K and P = 40000 bar. If the stable assemblage is **Mica + Gt + Mag + Cpx + Cpx + law + coe + ru**, you have configured the problem correctly, otherwise ask for help.

iv) Rename the print output file **my_project.prn** to **simple.prn**, so that you can compare your results with subsequent calculations.

Why are there two phases identified as **Cpx**?

Towards the end of the output MEEMUM writes the bulk composition in both molar and mass units. Thus, a simple way of converting an analysis reported in mass units, as obtained by XRF analysis, to molar units, which are generally more convenient for phase equilibrium modelling, is to run MEEMUM with the mass composition and copy the molar composition from its output.

Step 3: Phase diagram sections, VERTEX (Figure 1)

VERTEX is the phase diagram calculator.

Run VERTEX.

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(CHA)**, i.e., the most stable hydroxylated phase in the calculation.

If you wish to improve the resolution of your section change **x/y_nodes** in **perplex_option.dat** from **default** to **40 80** and repeat the calculation with VERTEX.

NOTE: because the **solution_names** option in **perplex_option.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

WERAMI extracts data from calculations made with VERTEX. In operational mode 1 (properties at specified conditions) it is essentially equivalent to MEEMUM; however, WERAMI interpolates between results calculated by VERTEX, whereas MEEMUM computes the stable phase relations directly. To see the consequences of this difference, run WERAMI, choose operational mode 1, specify T = 1000 K and P = 40000 bar, and compare the output from WERAMI with the output in **simple.prn** from MEEMUM that you obtained earlier (Step 7).

Step 6: WERAMI, using mineral compositions for thermobarometry

If you are interested in physical properties more than thermobarometry, try making 3-d surface plots of properties such as density (property choice 2), heat capacity (property choice 3), or seismic wavespeed (property choices 12-14) and skip the remainder of this step.

To illustrate the use of WERAMI for thermobarometry find the conditions at which mica [**Mica(CF)**] with a molar phengite-content (= Mg + Fe) of **0.87±0.02** coexists with garnet [**Gt(HP)**] with a grossular-content of **0.36±0.02**.

i) quit operational mode 1 by entering **99 99**, select operational mode 2 (**properties on a 2d grid**), choose property 8 (**composition of a solution**). Enter **Mica(CF)**, answer **yes** to the **Define the composition in terms of the species** prompt and specify the composition (C_Mica = **1 cel + 1 fcel**, cel and fcel are the Mg- and Fe-phengite endmembers, the coefficients on cel and fcel are the **weighting factors** requested by WERAMI). Repeat the process for Gt(HP), i.e., specify the composition (C_Gt = **1 gr**, gr is the grossular endmember. In general defining compositions in terms of species fractions is easier than using components (the alternative offered by WERAMI if you answer **no** to the **Define the composition in terms of the species** prompt), however the use of species requires knowledge of the solution models endmembers. See Solution Composition Variables for more explanation.

ii) Terminate property selection by entering **0**, and press **<enter>** in response to the remaining prompts. WERAMI issues several warnings, **warning ver178** is only relevant for seismic velocity calculations, **warning ver637** concerns a cosmetic detail that can be safely corrected in this case, if desired, by setting the **warning_ver637** option to **F** (if you don't do this, the mica compositional contours will be stepped in phase fields where two pyroxenes coexist). Once WERAMI completes the calculation it prints the ranges for the computed properties and indicates the name of the file that contains the output, e.g., **my_project_1.tab.**

iii) To visualize the data in **my_project_1.tab** 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). With whichever program you choose, make contour plots 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** in the MATLAB console after making the first plot. The **perple_x_plot** MATLAB script allows more flexibility than **perplex_simple_plot**, but has no special utility in this example.

iv) Under the assumption that the uncertainty in mineral composition is your only source of error (it isn't) sketch the error ellipse for your estimate of the conditions at the Mica and Garnet were in equilibrium.

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.

i) To improve the appearance of the plot, open **perplex_option.dat** and set the values of the **fancy_cumulative_modes** and **warning_ver637** keywords to **T** and **F**, respectively.

ii) Start WERAMI and select 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(bar) = 25144 − 22.4 T + 0.044 T^2 (fit for T = 673-1400 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 that 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. On completion WERAMI summarizes the ranges for the modes and writes the output in files for two different plot formats (**my_project_2.tab** and **my_project_2.plt**); the console output indicates which format can be read by which plotting program.

iii) Plot the result. A prominent feature of the plot are the erratic proportions of the 2 Cpx phases that coexist at temperatures between 675 to 900 K. The reason for this behavior is that VERTEX does not necessarily identify/list coexisting phases of an immiscible solution in the same order and under the "modes of all phases" WERAMI has no criteria for sorting these phases, thus the modal abundances of the augitic and omphacitic Cpx phases may be interchanged along the two curves representing Cpx. The problem can be resolved by graphical editing or by plotting the modes of each phase individually (**property choice 5**).The problem emerges less often in 1-dimensional calculations; so actually making the calculation along the 1-dimensional path of interest in VERTEX, rather than trying to extract the data from a 2-d calculation, as done here, may yield better results.

iii) 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. For example, extract the stable assemblage at 675 K and 30070 and use this information to resolve the ambiguity of the phase field labelling (if there is any).

Step 8: Bulk compositional (X) variables

That the bulk composition of the system is unconstrained is implicit in the Perple_**X** program CONVEX, in VERTEX you have the option of defining up to two explicit compositional variables. In contrast to CONVEX, where the compositional variables correspond to the components of the system, in VERTEX the compositional variables are arbitrarily defined, e.g., a variable can be chosen to describe how phase equilibria change when basalt is added to a granitic system. Here I suggest that you make an isobaric (P = 4 GPa) *T-X* phase diagram section for the metabasalt composition specified in Step 5 to show the influence of the volatile components (H2O, CO2) on its phase relations. If you have an abundance of time run BUILD to set up the problem; otherwise it is much more efficient to edit the input file from Step 1 to read:

```
begin thermodynamic component list
NA2O    2    0.32800    0.32800    0.00000  molar amount
MGO     2    1.62300    1.62300    0.00000  molar amount
AL2O3   2    1.49700    1.49700    0.00000  molar amount
K2O     2    0.58E-01   0.58E-01   0.00000  molar amount
CAO     2    2.25800    2.25800    0.00000  molar amount
TIO2    2    0.13800    0.13800    0.00000  molar amount
FEO     2    1.37000    1.37000    0.00000  molar amount
SIO2    2    7.49000    7.49000    0.00000  molar amount
H2O     2      0        1.46000    0.00000  molar amount
CO2     2      0        0.65900    0.00000  molar amount
end thermodynamic component list
```

The 2nd column indicates the number (2) of compositions to be read by VERTEX, the 3rd column is the volatile-free bulk composition (C0), and the 4th column is the volatile-bearing composition (C1). The bulk composition of the system is computed as C = C0 * [1-X(C1)] + C1*X(C1), i.e., a closed composition space, by setting the closed_c_space option to F (false) you can make C = C0 + C1*X(C1), which would simplify the composition (C1) entered in the 4th column (i.e., the first eight rows of the fourth column would be replaced by zeros).

Additional/Alternative Exercises:

Open system devolatilization (phase fractionation)

Open **perplex_option.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(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 8 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 H_2O, CO_2, and O_2 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 H_2O, CO_2, and CH_4 in the fluid along the geotherm. Plot the species abundances.

Open **perplex_option.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.

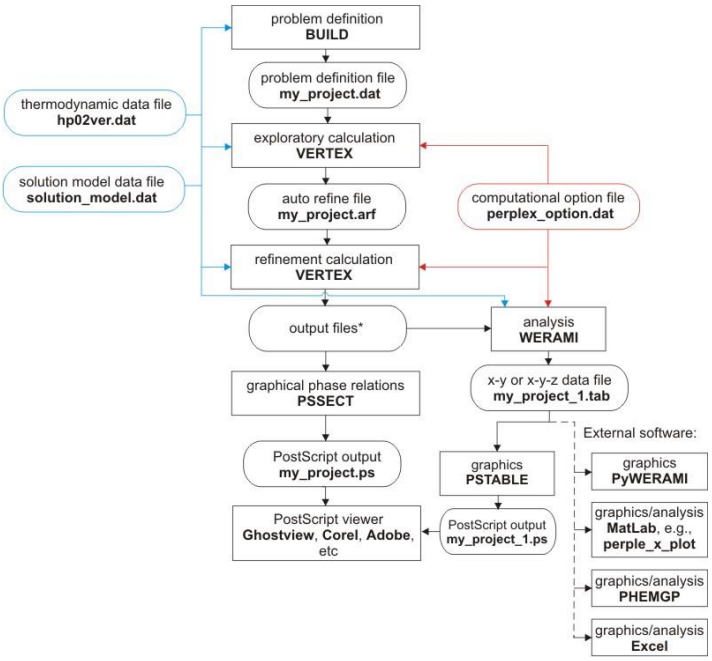

Figure 2 Program/file structure for Convexhull optimization calculations (Solution model exercises 1-3).

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). The files referred to here are in additional_exercise_files. 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(Na), z(Ca) and z(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 $G_{excess} = W_{py\text{-}gr}\, y_{py}\, y_{gr}$ (with $W_{py\text{-}gr}$ = 33000 J/mol). It may be helpful to copy the model the "**T**" (talc) 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(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 **CTRANSF** so that the data base components correspond to the endmember compositions (e.g., transform MgO to $Mg_3Al_2Si_3O_{12}$ 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