

# Pisa 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

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 [pisa\\_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).

This tutorial description and script are included in the [pisa tutorial.zip](#) file archive.

## 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 electrolytic C-O-H fluid rather than as a binary H<sub>2</sub>O-CO<sub>2</sub> 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.

### Step 1: Run BUILD (Figure 1)

**NOTE 0:** 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 console window, now is the time to do so (see Step 3 of the [WINDOWS](#), [MAC](#), or [LINUX](#) setup instructions).

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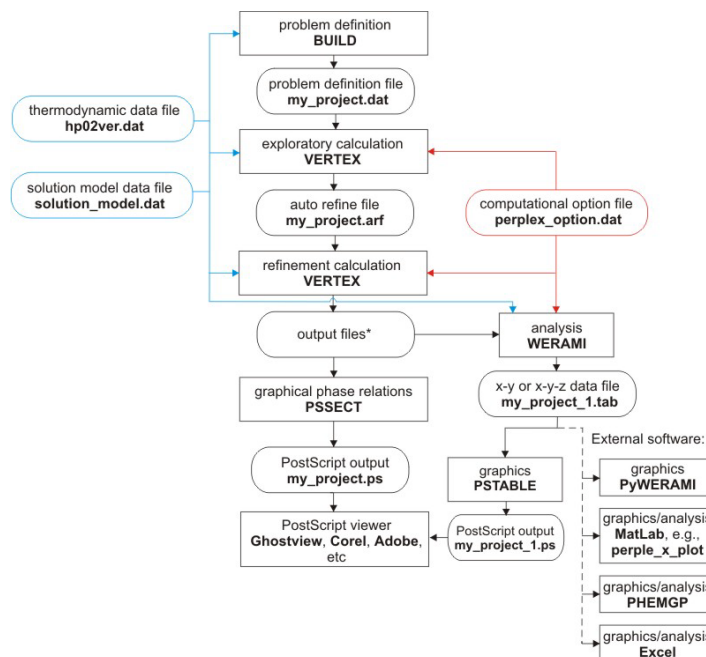


Figure 1. Program/file structure for the tutorial calculation with VERTEX. We will use **DEW17HP622ver\_oxides.dat** instead of the default thermodynamic data file (**HP02ver.dat**) indicated in the flow chart.

**NOTE 1:** 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 2:** 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 3:** 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.

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 the molar composition: Na<sub>2</sub>O 0.328; MgO 1.623; Al<sub>2</sub>O<sub>3</sub> 1.497; K<sub>2</sub>O 0.058; CaO 2.258; TiO<sub>2</sub> 0.138; FeO 1.370; SiO<sub>2</sub> 7.490; H<sub>2</sub>O 1.460; CO<sub>2</sub> 0.659.

Use the [DEW17HP622ver\\_oxides.dat](#) thermodynamic data file and the [perplex\\_option.dat](#) option file. This data file is a hybrid of the DS6.22 THERMOCALC data file for solids and molecular species and the 2017 version of the DEW model for aqueous species. This data file uses oxide components, normally for calculations that include electrolytic fluids is best to use elemental components (e.g., DEW17HP622ver\_elements.dat). If you are not interested in electrolytic fluids use the [HP622ver.dat](#) thermodynamic data file.

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

Do not (for the moment) exclude any phases.

Answer yes to the use solution models prompt. Specify the [solution\\_model.dat](#) solution model file and select the models: **Chl(W)** [chlorite], **Mica(CHA)** [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** [talca], **Do(HP)** [dolomite], **M(HP)** [magnesite], and **Gt(W)** [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, without redox

MEEMUM is an interactive Free 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.

i) By default Perple\_**X** includes all chemically relevant endmembers and/or species that are present in the thermodynamic data file in a calculation. Normally, it is best not to exclude any of these endmembers and/or species from 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. To save time here, [pisa\\_excluded\\_species.txt](#) contains a list of phases and/or species that should be excluded for the present exercise. Open [pisa\\_excluded\\_species.txt](#) in an editor such as WORDPAD. Copy this list into your problem definition file **my\_project.dat** after the “**begin excluded phase list**” keyword; save the modified file.

ii) Edit the option file (**perplex\_option.dat**): change the value of **solution\_names** from **default** to **abb** and, for the moment, suppress output of electrolytic speciation by setting the value of **aq\_output** to **F**; save your edits.

iii) 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.

What is the significance of the two phases identified as **Cpx**?

**NOTE:** 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: Run MEEMUM, with redox but wrong

Although we have assumed the bulk composition can be described entirely in terms of reduced oxides, it does not follow that oxygen cannot disproportionate among the phases of the system. Disproportionation could not occur in the previous calculation because our choice of components was incapable of describing variation in redox state. To remove this limitation, we now specify  $O_2$  (“excess oxygen”), 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.

i) Edit **my\_project.dat**: at the end of the list of thermodynamic components add the line “ $O_2 \ 1 \ 0.$ ”, the first five characters are reserved for the component name, the rest of the information has no particular format, the 1 indicates the number of compositions that follow, the 0. is the amount of excess oxygen in the bulk composition; save your edits.

ii) Run MEEMUM, the program issues to intrusive (i.e., interactive) warnings to which you must answer yes in order to continue. Intrusive warnings are designed to force the user to acknowledge probable bad practice, as is indeed the case here. Specifically, **Perple\_X** requires that the sum of the molar amounts of the components in any phase must be greater than zero (this is not a thermodynamic constraint, rather it is related to a bookkeeping issue in **Perple\_X**). Our C-O components are currently CO<sub>2</sub> and O<sub>2</sub>, thus the composition of graphite and diamond, C, is 1 CO<sub>2</sub> - 1 O<sub>2</sub>, and the total amount of the components in both phases is 0. Continue, answering no (or simply press enter) to all prompts until prompted for physical conditions, enter  $T = 673$  K and  $P = 40000$  bar. The stable assemblage should be **F (fluid) + Mica + Gt + Mag + Cpx + Cpx + law + coe + ru**.

Verify that the bulk excess oxygen content is zero, i.e., the system has neither been reduced nor oxidized. What is the speciation of the fluid phase? What are the ferric/ferrous ratios in the pyroxene phases (these can be computed from either the phase composition or the structural formulae sections of the output)? How did a methane-rich fluid form from a bulk composition that contained only CO<sub>2</sub>? Due to the Principle of Maximum Astonishment, reduced-fluids get a lot of attention from metamorphic petrologists; however, from a mass-balance perspective it is evident that devolatilization must primarily generate oxidized fluids. Ferric iron is indeed ubiquitous and its formation by oxidation of ferrous iron, should that actually happen during fluid generation, requires reduction elsewhere. Here, this reduction is largely accomplished by reducing CO<sub>2</sub> in carbonate to CH<sub>4</sub> in the fluid. Such processes are plausible in nature, but, by excluding graphite and diamond here, we have effectively eliminated any alternative process.

#### Step 4: Run CTRANSF, component transformation

To correct the error in Step 3, transform the oxide carbon component (CO<sub>2</sub>) specified in the **DEW17HP622ver\_oxides.dat** data file to the elemental carbon component C. Best practice is to use elemental components for any element that may be stable as a species or phase in elemental form, therefore, as the fluid may contain the H<sub>2</sub> species, we may as well transform H<sub>2</sub>O to H<sub>2</sub> while we are doing transformations. The best way to do component transformations is with the **Perple\_X** program **CTTRANSF**.

i) Run **CTTRANSF**, enter **DEW17HP622ver\_oxides.dat** as the file to be converted.

ii) Replace CO<sub>2</sub> with C, when asked for other components in CO<sub>2</sub> enter O<sub>2</sub>. The amounts of the old components (CO<sub>2</sub> and O<sub>2</sub>) in C are, respectively, 1 and -1 (i.e.,  $C = CO_2 - 1 O_2$ ). Replace H<sub>2</sub>O with H<sub>2</sub> (i.e.,  $H_2 = H_2O - \frac{1}{2} O_2$ ). Press enter when prompted for additional transformations, CTRANSF will then create a new thermodynamic data file, named **ctransf.dat**, with the transformed components (inspect it if you like).

#### Step 5: Run MEEMUM, with redox done right

i) Edit **my\_project.dat**: on line 1, replace **DEW17HP622ver\_oxides.dat** with **ctransf.dat**; convert the molar amounts of the oxides CO<sub>2</sub> and H<sub>2</sub>O to molar amounts of the elemental components C, H<sub>2</sub>, and O<sub>2</sub>; change the names of CO<sub>2</sub> and H<sub>2</sub>O in the list of thermodynamic components to C and H<sub>2</sub>; enter the converted amounts to C, H<sub>2</sub>, and O<sub>2</sub> after the component names.

ii) Run MEEMUM with project **my\_project** and  $T = 673$  K and  $P = 40000$  bar.

The stable assemblage should be **Mica + Gt + Mag + Cpx + Cpx + law + coe + ru + diam**. Boring, unless you like diamonds, but correct. What is the volumetric mode of diamond?

#### Step 6: Simple back-calculated electrolytic speciation with MEEMUM

Electrolytic fluid speciation can be calculated in **Perple\_X** in two different ways: **simple back-calculated speciation** or **lagged-speciation**. Simple back-calculation ([Galvez et al. 2015](#)) estimates

the electrolytic speciation that the fluid would need to have in order to be equilibrated with the predicted mineralogy, but it does not account for solute mass balance. This is a useful approximation for solution chemistry in rock-dominated hydrothermal systems (i.e., where solute mass  $\ll$  rock mass).

- i) In **perplex\_option.dat**: change the value of **aq\_output** from **F** to **T**.
- ii) Copy **my\_project.dat** to **simple.dat**.
- iii) Change the second line of in **simple.dat** from **no\_print** to **print**, this will cause MEEMUM to echo the console output to the file **simple.prn**.
- iv) Run MEEMUM with project **simple** and  $T = 1000$  K and  $P = 40000$  bar. Terminate MEEMUM and open **simple.prn**.

What is the true (optimized) speciation of the fluid indicated in “Phase speciation” section of the output? Examine the hypothetical back-calculated speciation of the fluid listed at the end of the output. What is the hypothetical total solute molality? Would the fluid be acidic ( $\Delta_{\text{pH}} = \text{pH} - \text{the neutral pH}$ )? What would the mass fraction of  $\text{SiO}_2$  be in the fluid? The hypothetical solute speciation would have relatively minor effect on closed system devolatilization; however if mass transport is of concern, the calculation indicates that the solute mass is significant.

#### Step 7: Lagged electrolytic speciation with MEEMUM

The true (i.e., thermodynamically rigorous) electrolytic fluid speciation can be obtained in Perple\_X by **lagged-speciation** ([Connolly & Galvez 2018](#)). In lagged speciation, the true solute speciation is approximated by iteratively updating the fluid compositions used during optimization by back-calculation. In the context of the lagged-speciation output, the back-calculated result is obtained after the last iteration, this differs from simple back-calculated speciation in that the latter is the result without iteration.

- i) In **perplex\_option.dat**: change the value of **aq\_lagged\_speciation** from **default** to **T**.
- ii) Run MEEMUM with project **my\_project** and  $T = 1000$  K and  $P = 40000$  bar.

Note that in the phase composition section the fluid now contains solute components. Examine the true (optimized) fluid speciation in the “Phase speciation” section of the output, this speciation includes pseudo-species that indicate pH, total solute molality, etc. The speciation is repeated at the end of the output in the same form as was done for simple back-calculation in Step 6; however here the last back calculated result and the optimized results are compared. The comparison is provided so that the user can verify that the lagged speciation algorithm has converged. Comparison with the speciation in **simple.prn** demonstrates that simple back-calculation provides an excellent approximation to the true speciation.

#### Step 8: Phase diagram sections, VERTEX (Figure 1)

VERTEX is the phase diagram calculator.

- i) Because lagged speciation calculations are slow and not possible over the entire P-T coordinate frame specified in Step 1, edit **perplex\_option.dat** change the value of **aq\_lagged\_speciation** from **T** to **F**. If you want to continue with lagged speciation, I suggest you modify the “Open system devolatilization exercise” listed below under “Additional Exercises” to use lagged speciation with the C-O-H component data file (**ctransf.dat**) created in Step 4.

ii) Also set the option **interim\_results** to **man**, this will allow you to evaluate interim results with the programs PSSECT and WERAMI. By default, **interim\_results** is set to **auto**, in which case interim results can only be viewed while VERTEX is running.

iii) Run VERTEX.

#### Step 9: 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(W)**, 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 **10 60** 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 10: 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 6).

#### Step 11: 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 ( $= \text{Mg} + \text{Fe}^{2+}$ ) 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(W)**, answer **yes** to the **Define the composition in terms of the species** prompt and specify the composition ( $C_{\text{Mica}} = 1 \text{ cel} + 1 \text{ fcel}$ , 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(W), i.e., specify the composition ( $C_{\text{Gt}} = 1 \text{ gr}$ , 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. Here, the use of components to define compositions would require a correction for the fact that as the sole Fe-bearing component, FeO must represent total iron content and therefore that ferrous iron content in garnet or mica must be computed as  $n(\text{FeO}') = n(\text{FeO}) - [n(\text{O}_2) - n(\text{H}_2)/2]/2$ , where  $[n(\text{O}_2) - n(\text{H}_2)/2]$  is the excess  $\text{O}_2$  in mica that is not bound to H. 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 12: 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  $P(\text{bar}) = 25144 - 22.4 T + 0.044 T^2$  (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. 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 instability is that the proportions of immiscible phases can be extremely sensitive to physical conditions, but WERAMI estimates these by linear interpolation of the relatively sparse data output by VERTEX. The numerical noise could be eliminated by making the calculation along a 1-dimensional path in VERTEX, rather than trying to extract the data from a 2-d calculation as done here.

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).

iv) 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. To do this is to choose property #8 (composition of a solution) for each species of COH-Fluid; an easier alternative is to choose property #40, but in this case the molecular species abundances are diluted by the putative solute load obtained by simple back-calculation. 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.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 H<sub>2</sub>O, CO<sub>2</sub>, and O<sub>2</sub> 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<sub>2</sub>O, CO<sub>2</sub>, and CH<sub>4</sub> 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.



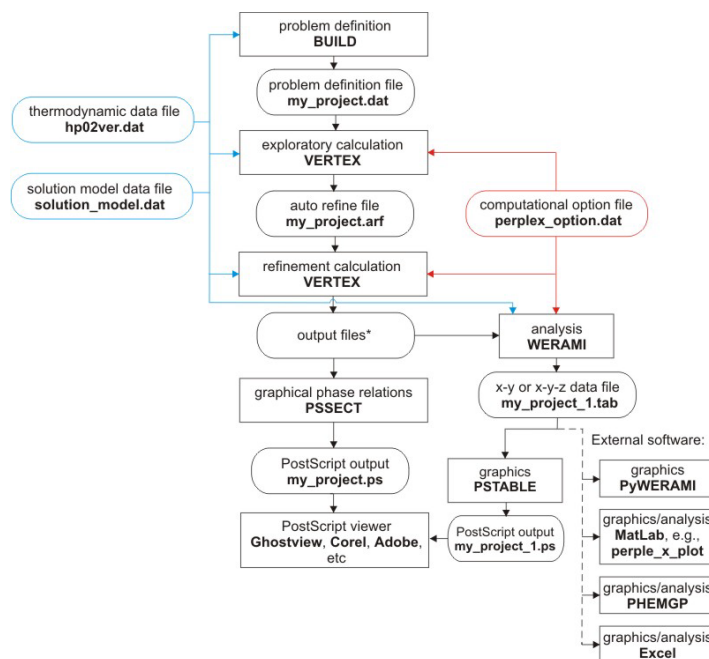


Figure 2 Program/file structure for Convexhull optimization calculations (Solution model exercises 1-3).

### 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). 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  $W_{\text{py-gr}} = 33000$  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  $X(\text{C1})-$

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  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  as saturated components so that remaining thermodynamic components are identical to the projected endmember compositions (e.g., after “projection” through  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ ; the composition of pyrope is MgO, etc.)
- 2) Transform the data base components using **CTTRANSF** 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