

Perplex Tutorial 1

Basics

Perplex is a collection of programs, each designed to accomplish a different task. These are unix programs (although there are versions for Windows as well). You run them from the command line. To get a command line on Mac OSX, you run Terminal (which is in Applications/Utilities). Do not double-click on the program from within the graphical interface: if you do, the programs may or may not work correctly.

For simplicity, the programs will only read and write files from their own directory. You should be supplied with a “template folder” that contains all the programs and datafiles needed to run these tutorials. The most effective thing to do is to make a duplicate of this whole folder for each task, in a location to which you have write access, such as the Desktop (the template itself might not be in a user-writeable location).

Once you have created a duplicate of the template folder and its contents, make that folder your “working directory”. If you named the duplicate “task1folder” and it were located on your Desktop, then at the command line (on Mac OS X) you would type

```
cd $HOME/Desktop/task1folder
```

to move (or change directory) into the folder. Now you are ready to run Perplex.

Note that your computer may be set up differently from these examples - ask your instructor if necessary.

Programs in Perplex

This tutorial is based on the version of Perplex and datafiles available on March 7, 2007. In particular, these are based on Perplex '06 not Perplex '07. The programs you will use are:

- **BUILD** - this makes the datafile that tells VERTEX how to setup the calculation. You will spend most of your effort on BUILD.
- **VERTEX** - this does the calculation and saves the results.
- **PSVDRAW** - this takes the plotfile output from VERTEX and makes a postscript plot from it. You can specify options to highlight particular aspects of the file.
- *Adobe Illustrator CS2* - this opens the postscript file into something you can edit for legibility, and save as a PDF.

There are others, but you should not need to use them. The data files the program needs in order to run are these. Note that these files must be in the same directory as the programs, and need to have the right line endings for the operating system you are using.

- *hp02ver.dat* - This is the thermodynamic database of Holland and Powell (2002). You could run Perplex with other databases that you can download from the Perplex website.
- *newest_format_solut.dat* - This is the file with all the possible solution models that relate free energy of a phase to its composition. Note that many phases have multiple possible solution models that you might choose. Read the file for some guidance as to which is best for your problem.

Task 1 - Making a ternary phase diagram

This is one of the simplest tasks in Perplex. We will make a simple ternary phase diagram without any solid solution phases, and we will show how it changes with a change in conditions.

(Note: If you merely type stuff in by following this guide, you won't learn anything. You are expected to read all the prompts and ask questions if there are some that you don't understand. In later tasks you will be expected to redo this, changing your responses in various ways to achieve other results. If you don't actually read these, then you will be confused later.)

Building the run file

First run BUILD:

```
./build
```

NO is the default (<cr>) answer to all Y/N prompts (This is the font I will use for text the program will print out)

```
Enter name of computational option file to be created,
< 100 characters, left justified [default = in]:
task1.txt
```

```
Enter thermodynamic data file name, left justified, [default = hp02ver.dat]:
```

(Note that you can just hit return to accept any default option, and that NO is the default for all "Y/N" choices). Hit return here.

```
The current data base components are:
```

```
NA2O  MGO  AL2O3  SiO2  K2O  CAO  TiO2  MNO  FEO  NIO  ZRO2  CL2
O2     H2O  CO2
```

```
Transform them (Y/N)?
```

N

```
Calculations with a saturated phase (Y/N)?
```

```
The phase is:  FLUID
```

```
Its compositional variable is: Y(CO2), X(O), etc.
```

Y

```
Select the independent saturated phase components:
```

```
H2O  CO2
```

```
Enter names, left justified, 1 per line, <cr> to finish:
```

For C-O-H fluids it is only necessary to select volatile species present in the solids of interest. If the species listed here are H2O and CO2, then to constrain O2 chemical potential to be consistent with C-O-H fluid speciation treat O2 as a saturated component. Refer to the Perple_X Tutorial for details.

H2O

CO2

```
Calculations with saturated components (Y/N)?
```

N

```
Use chemical potentials, activities or fugacities as independent
variables (Y/N)?
```

N

```
Select thermodynamic components from the set:
```

```
NA2O  MGO  AL2O3  SiO2  K2O  CAO  TiO2  MNO  FEO  NIO  ZRO2  CL2
```

O2
 Enter names, left justified, 1 per line, <cr> to finish:
CAO
MGO
SIO2

Select fluid equation of state:

- 0 - X(CO2) Modified Redlich-Kwong (MRK/DeSantis/Holloway)
- 1 - X(CO2) Kerrick & Jacobs 1981 (HSMRK)
- 2 - X(CO2) Hybrid MRK/HSMRK
- 3 - X(CO2) Saxena & Fei 1987 pseudo-virial expansion
- 4 - Bottinga & Richet 1981 (CO2 RK)
- 5 - X(CO2) Holland & Powell 1991, 1998 (CORK)
- 6 - X(CO2) Hybrid Haar et al 1979/CORK (TRKMRK)
- 7 - f(O2/CO2)-f(S2) Graphite buffered COHS MRK fluid
- 8 - f(O2/CO2)-f(S2) Graphite buffered COHS hybrid-EoS fluid
- 9 - Max X(H2O) GCOH fluid Cesare & Connolly 1993
- 10 - X(O) GCOH-fluid hybrid-EoS Connolly & Cesare 1993
- 11 - X(O) GCOH-fluid MRK Connolly & Cesare 1993
- 12 - X(O)-f(S2) GCOHS-fluid hybrid-EoS Connolly & Cesare 1993
- 13 - X(H2) H2-H2O hybrid-EoS
- 14 - EoS Birch & Feeblebop (1993)
- 15 - X(H2) low T H2-H2O hybrid-EoS
- 16 - X(O) H-O HSMRK/MRK hybrid-EoS
- 17 - X(O) H-O-S HSMRK/MRK hybrid-EoS
- 18 - X(CO2) Delany/HSMRK/MRK hybrid-EoS, for P > 10 kb
- 19 - X(O)-X(S) COHS hybrid-EoS Connolly & Cesare 1993
- 20 - X(O)-X(C) COHS hybrid-EoS Connolly & Cesare 1993
- 21 - X(CO2) Halbach & Chatterjee 1982, P > 10 kb, hybrid-EoS
- 22 - X(CO2) DHCORK, hybrid-EoS
- 23 - Toop-Samis Silicate Melt
- 24 - f(O2/CO2)-N/C Graphite saturated COHN MRK fluid
- 25 - H2O-CO2-NaCl Aranovich and Haefner 2004

5

There are lots of choices here; option 5 is a good one for many calculations, unless you have a good reason to choose another. There is guidance on these options in the Perplex documentation.

Specify computational mode:

- 1 - Unconstrained minimization [default]
- 2 - Constrained minimization on a grid
- 3 - Output pseudocompound data
- 4 - Phase fractionation calculations

Unconstrained optimization should be used for the calculation of composition, mixed variable, and Schreinemakers diagrams, it may also be used for the calculation of phase diagram sections for a fixed bulk composition. Gridded minimization can be used to construct phase diagram sections for both fixed and variable bulk composition. Gridded minimization is preferable for the recovery of phase and bulk properties.

1

The data base has P(bar) and T(K) as default independent potentials. Make one dependent on the other, e.g., as along a geothermal gradient (y/n)?

N

Specify number of independent potential variables:

- 0 - Composition diagram [default]
- 1 - Mixed-variable diagram
- 2 - Sections and Schreinemakers-type diagrams

0

Constrain bulk composition (as in pseudosections, y/n)?

N

Do you want a print file (Y/N)?

Y

Enter the print file name, < 100 characters, left justified [default = pr]:

task1print.txt

Print dependent potentials for chemographies (Y/N)?

Answer no if you do not know what this means.

N

Do you want a plot file (Y/N)?

Y

Enter the plot file name, < 100 characters, left justified [default = pl]:

task1plot.txt

Exclude phases (Y/N)?

N

Do you want to treat solution phases (Y/N)?

N

Enter calculation title:

Task 1

Specify values for:

P(bar) T(K) Y(CO2)

For calculation 1, enter zeros to finish.

3000 830 0.2

Specify values for:

P(bar) T(K) Y(CO2)

For calculation 2, enter zeros to finish.

3000 840 0.2

Specify values for:

P(bar) T(K) Y(CO2)

For calculation 3, enter zeros to finish.

3000 865 0.2

Specify values for:

P(bar) T(K) Y(CO2)

For calculation 4, enter zeros to finish.

0 0 0

Now you are done with BUILD. Let's take a look at the file you made. Type

more task1.txt

and peruse the document, hitting space until you reach the end. If you want to edit the file to see what parts control which behavior, or to make a similar run with slight changes, you can use a text editor like TextWrangler (free for the Mac) or Notepad (Windows) or you can use pico in the Terminal (but don't use MS Word or TextEdit):

pico task1.txt

Hit [Control]-X to stop editing the file. Don't save any changes for now.

Doing the calculations

Run VERTEX to actually do the calculations:

./vertex

Output options are currently set as:

Keyword:	Value:	Permitted values [default]:
average	on	off [on] both
compositions	mol	wt [mol]
proportions	vol	wt [vol]
interpolation	on	off [on]
extrapolation	on	off [on]
vrh_weighting	0.5	0->1 [0.5]
bad_number	0.	[0.0]
solvus_tolerance	0.100	0->1 [0.10], = 1 => off
zero_mode	0.1E-05	0->1 [1e-6], < 0 => off

To change these options edit or create the file perplex_option.dat

See: www.perplex.ethz.ch/perplex_options.html

Enter computational option file name (i.e. the file created with BUILD), left justified:

task1.txt

Reading thermodynamic data from file: hp02ver.dat

Writing print output to file: task1print.txt

Writing plot output to file: task1plot.txt

Reading solution models from file: none requested

****warning ver052**** rejecting tipc ; excluded or invalid composition.

****warning ver052**** rejecting mthm ; excluded or invalid composition.

****warning ver052**** rejecting qfm ; excluded or invalid composition.

****warning ver052**** rejecting tbi ; excluded or invalid composition.

****warning ver052**** rejecting fbr ; excluded or invalid composition.

****warning ver052**** rejecting fchum ; excluded or invalid composition.

****warning ver052**** rejecting fphA ; excluded or invalid composition.

****warning ver052**** rejecting fper ; excluded or invalid composition.

****warning ver052**** rejecting fatg ; excluded or invalid composition.

```
**warning ver052** rejecting sil8L ; excluded or invalid composition.
```

```
**warning ver052** rejecting fa8L ; excluded or invalid composition.
```

Summary of valid make definitions:

	MGO	SIO2	CAO	CO2
odo	0.50	0.00	0.50	1.00
fo8L	4.00	2.00	0.00	0.00
q8L	0.00	4.00	0.00	0.00

Done generating pseudocompounds (total: 0)

```
Computing the compositional phase relations at condition 1
cycle 1 1 1
cycle 2 2 2
cycle 3 3 3
cycle 4 4 4
Computing the compositional phase relations at condition 2
cycle 1 1 1
cycle 2 2 2
cycle 3 3 4
cycle 4 5 5
cycle 5 6 6
Computing the compositional phase relations at condition 3
cycle 1 1 1
cycle 2 2 3
cycle 3 4 5
cycle 4 6 7
cycle 5 8 8
```

Viewing the results

Good! Now you have completed the calculations. You can see the text output in the file you specified:

```
more task1print.txt
```

Note that it shows the stable assemblage at each set of conditions. In order to get a diagram of the results, you can make a postscript file from the plot file:

```
./psvdraw
```

Output options are currently set as:

Keyword:	Value:	Permitted values [default]:
average	on	off [on] both
compositions	mol	wt [mol]
proportions	vol	wt [vol]
interpolation	on	off [on]
extrapolation	on	off [on]
vrh_weighting	0.5	0->1 [0.5]
bad_number	0.	[0.0]
solvus_tolerance	0.100	0->1 [0.1] = 1 => off

```
zero_mode      0.1E-05      0->1 [1e-6], < 0 => off
```

To change these options edit or create file `perplex_option.dat`

See: www.perplex.ethz.ch/perplex_options.html

Enter the Perple_X plot file name:

task1plot.txt

PostScript will be written to file: `task1plot.ps`

Draw tielines (y/n[recommended])?

y

Now the results are saved in a file called `task1plot.ps`. If you double-click this file on the Mac, it will open in *Preview*, and convert to PDF, but this process fails to convert any text because the postscript that PSVDRAW makes is not really valid. The best thing to do is drag the file into *Adobe Illustrator*, which will preserve the text, and allow you to copy or edit things if you wish. When you do this, you should see the image at right (note that `odo` stands for “ordered dolomite”).

Turn in your **answers** to these questions:

1. What are the reactions shown here?
2. Can you find either of them on the T-X(CO_2) diagram attached?
3. Are they at the correct P-T-X(CO_2) conditions?

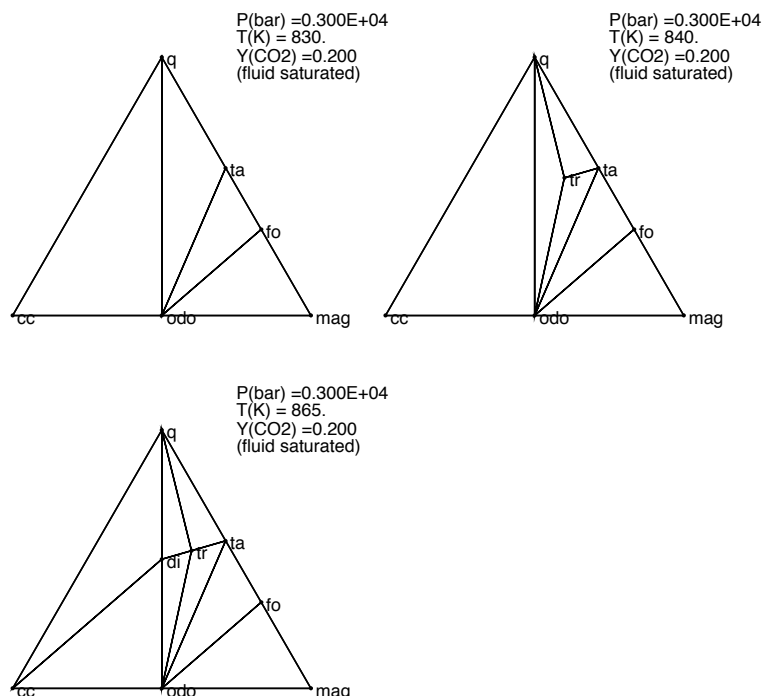
Go back and edit your `task1.txt` file. In between the lines:

```
begin excluded phase list
end excluded phase list
```

type “`odo`” (on its own line). Now re-run VERTEX and PSVDRAW.

4. Examine your output; how is it different?

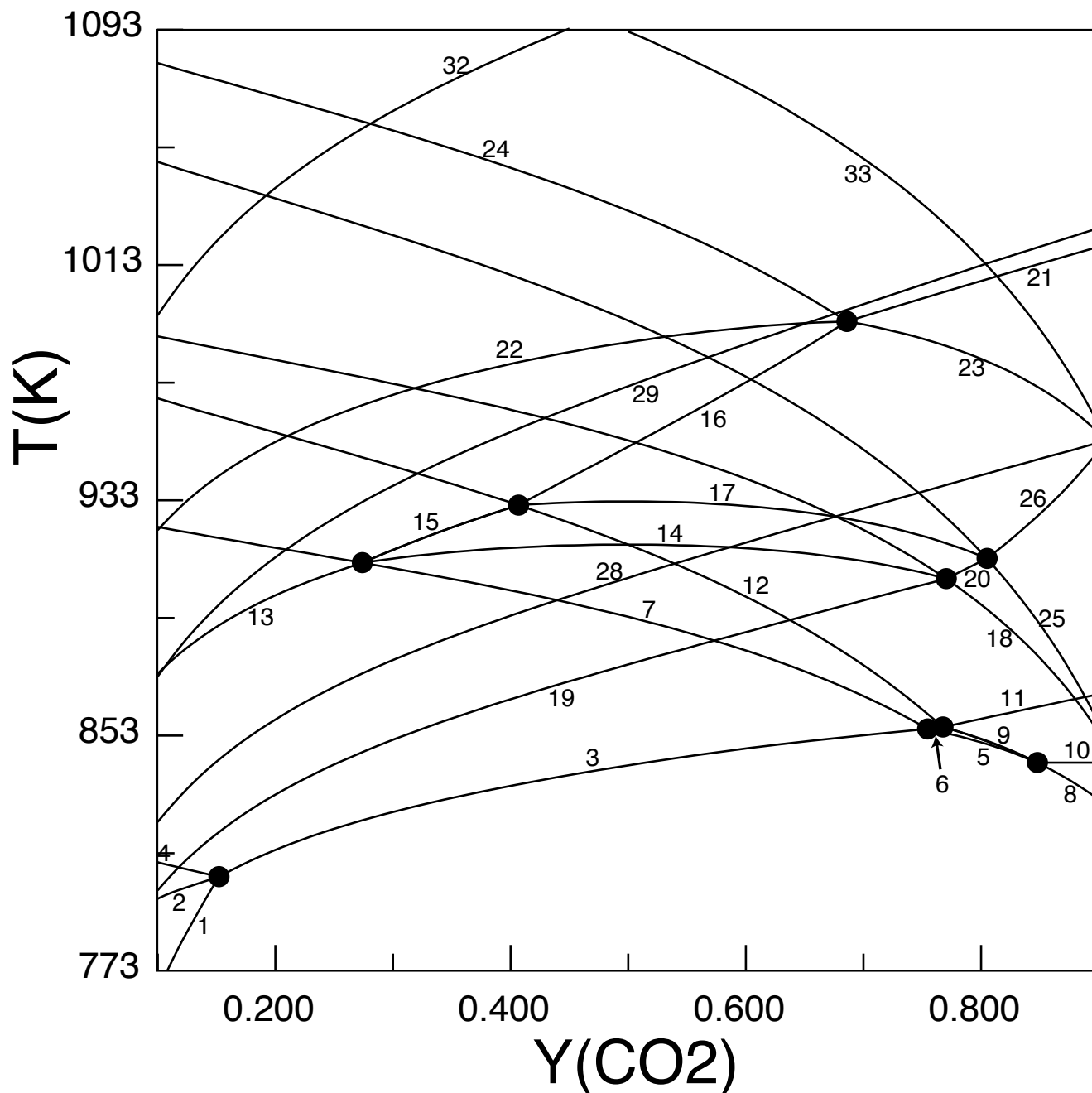
Finally, choose another reaction on the T-X(CO_2) diagram (try not to duplicate the points chosen by your classmates) and calculate the diagrams across that reaction as well, by adding more P-T-X lines near the end of the `task1.txt` file. Run VERTEX and PSVDRAW again. Turn in this final print file and plot, along with the answers to the above questions.



T-X(CO₂) Plot, P = 3000 bars

Reaction equations are written such that the high T(K) assemblage is on the right of the = sign.
Only reactions between 0.1 and 0.9 X(CO₂) are shown, and no solid solutions are used.

1: mag ta = atg	8: mag ta = en	15: odo anth = fo tr	22: odo tr = fo di	29: cc q = wo
2: mag atg = fo	9: mag anth = en	16: odo en = fo tr	23: odo tr = en di	30: di odo = cc fo
3: mag ta = fo	10: ta en = anth	17: odo anth = en tr	24: fo tr = en di	31: fo di cc = mont
4: atg = ta fo	11: mag en = fo	18: ta = anth q	25: anth = en q	32: mag = per
5: mag ta = anth	12: fo anth = en	19: odo ta q = tr	26: odo en q = tr	33: tr = q en di
6: mag anth = fo	13: odo ta = fo tr	20: odo anth q = tr	27: q mag = ta	
7: ta fo = anth	14: odo ta = anth tr	21: odo en = fo di	28: odo q = di	



Perplex Tutorial 2: P-T Diagrams

In contrast to the previous assignment, you will not be given detailed instructions. In this assignment, you will use Perplex to create P-T diagrams. First you will make a simple diagram, then some more complex ones.

Task 2 - Re-creating the Aluminum Silicate Phase diagram

Perplex refers to P-T diagrams as Schreinemakers diagrams; making them can be a very simple task in Perplex. You may wish to refer to assignment one for the prompts not covered here (give the same responses as in task 1).

Building the run file

1. Choose a different name than last time, perhaps "task2.txt"
2. For now, do not perform the calculations with either a saturated fluid phase or a saturated component.
3. When you choose oxide components, choose only Al_2O_3 and SiO_2 , since we're just looking for the stability of the Al_2SiO_5 minerals.
4. The computation mode should be unconstrained minimization.
5. For the number of independent potential variables, choose 2 (P & T).
6. Make temperature the x axis.
7. Perform the calculation from 200°C – 800°C, and from 1 kbar to 7 kbar (Note that Perplex wants temperature in Kelvins and pressure in bars)
8. Do not constrain bulk composition – we want a diagram that applies to *all* compositions in the SiO_2 – Al_2O_3 region.
9. Choose the long print file format, with all the trimmings (full reaction equations, stoichiometries, entropy & negative volume).
10. Make a plot file as well.
11. Don't exclude any phases.
12. Don't include any solution phases, either.

Results

Run VERTEX and PSVDRAW as usual to get the results. First, examine the print file you made. Note that the only phases being considered are those containing only Si, O, and Al.

Next the file tells you what is stable at the low-P, low-T corner of your calculation region. In this case, you could have either corundum + kyanite, or kyanite + quartz.

Question 1: What determines whether you have corundum + kyanite or kyanite + quartz?

Check out the P-T graph you made.

Question 2: If kyanite is apparently stable at such low grades, why do we think of kyanite as being a high-pressure mineral?

Next in the print file, each reaction (i.e., line of equilibrium) is described as a set of P-T coordinates. The S and -V (note the negative!) values are the ΔS and $-\Delta V$ of reaction, to be used in the Clausius-Clapeyron equation. They are listed as either reactants or products, and thus are negative or positive, respectively.

Question 3: What is the slope of the Ky–And reaction line (from the S & V values)?

Finally, the coordinates of the invariant point (triple point) are given. Note that it is listed as “(1–1)”.

Question 4: How do the coordinates of the invariant point compare to the commonly accepted (Holdaway & Mukhopadhyay, 1993) value of 3.75 ± 0.25 kbar and 504 ± 20 °C? Why might they be different?

In addition to the coordinates of the invariant point, the phases stable at the point are listed. Corundum is included, because in general the composition of the rock will in the SiO_2 – Al_2O_3 region will not be exactly Al_2SiO_5 . Why isn't it quartz along with the aluminum silicates? Try going into the build file (“task2.txt”) and switching the Al_2O_3 and SiO_2 lines., and then run VERTEX again. When you view the new print file, you'll see that quartz is now listed along with the aluminum silicates.

Task 3 - Enhancing the Aluminum Silicate Phase diagram

This diagram is fine for most purposes, but in reality the stability of these minerals is limited by other reactions at low temperatures. We'll redo the above work, but make it more realistic by including a water-rich fluid phase and assume quartz is present. These are good assumptions for almost any pelite likely to include enough aluminum to make an aluminum silicate.

Building the run file

1. Choose a different name than last time, perhaps “task3.txt”
2. This time, perform the calculations with a saturated H_2O –only fluid phase.
3. Also assume that quartz is present, and thus requires a saturated SiO_2 component.
4. Then when you choose oxide components, the only one left will be choose only Al_2O_3 .
5. The program will ask you for the sectioning value for Y(CO_2). Because you want a pure- H_2O phase, you should say zero.
6. Everything else should be as in tasks 1 and/or 2.

Results

Run VERTEX and PSVDRAW as usual to get the results. Examine the plot, and note the difference between this one and the previous one.

Question 5: Looking at the set of minerals (you may wish to look up formulas), what is the key chemical difference in the system that allows pyrophyllite and kaolinite to form?

Turn in your P–T graphs, and the above questions.

Task 4 - Make your own

Now do the same thing, but plot a P–T diagram for some other simple chemical system. Choose whether to have a fluid or not, and whether quartz is present or not (and possibly other oxide phases), and choose one or two other oxides. If you like, you can try to replicate a diagram in Spear (1993) (but I would suggest staying away from Fe and Mg). See what you get.

Turn in your diagram, with a brief description of your setup and a statement of what, if any, rock type your setup might apply to. Note particularly if there are phases that are listed as multiple end-members, but are in reality solid solutions.

Perplex Tutorial 3: Dealing with solid solutions

Task 5 - T-X_{MgO} diagram with solid solutions

Now for the first time we'll deal with solid solutions. Perplex deals with solid solutions by essentially creating a whole set of pseudocompounds (intermediate compositions), and treating each of them like a separate phase. Thus, if an olivine with composition Fo₈₀ has a lower free energy than Fo₈₅ at a particular P-T condition, then that Fo₈₀ olivine will be listed as the stable olivine.

We will plot the reactions that occur in the system K₂O-MgO-FeO-Al₂O₃-SiO₂-H₂O. However, to reduce the problem to one with only two thermodynamic components, water will be treated as a saturated phase, and we will project from SiO₂, Al₂O₃, and K₂O. This is like projecting onto the AFM triangle, but requiring that all the assemblages will coexist with quartz, aluminosilicate, and muscovite or K-feldspar.

Building the run file

1. Choose a different name than last time, perhaps "task5.txt"
2. This time, perform the calculations with a saturated **H₂O-only** fluid phase, so list only H₂O in the "independent saturated phase components" list.
3. Also assume that quartz, aluminum silicate, and muscovite/kspar are present, and thus require saturated SiO₂, Al₂O₃, and K₂O components (in that order).
4. When you choose oxide components, the only ones that will be variable are MgO and FeO; in order for the plots to all come out the same, put FEO first, and MGO second.
5. Choose unconstrained optimization again for the computation mode.
6. Choose "1 - Mixed-variable diagram" for the number of independent potential variables.
7. Temperature should be the vertical axis variable.
8. Plot the range of conditions: P=7 kbar, T= 500-650°C, and Y(CO₂)=0.0.
9. When BUILD asks if you want to exclude phases, you should say yes. It will ask if you want to be prompted for phases: you don't. Then enter only **afch1**. This will speed up the calculation by limiting the range of chlorite compositions Perplex will consider.
10. When BUILD asks if you want to treat solution phases, say yes, and accept the default solution model file name.
11. There will be a whole bunch of "... solution will not be considered" lines, because many solution endmembers are not present in the H₂O-SiO₂-Al₂O₃-K₂O-MgO-FeO system.
12. When it asks you to select phases from the list, these are various solution models for different minerals. Many minerals have more than one possible model you could choose. For simplicity, we'll choose all the Holland & Powell models, plus hCrd for cordierite. Here is the list:

```

Bio (HP)
Ch1 (HP)
Opx (HP)
Ctd (HP)
St (HP)
Gt (HP)
Sp (HP)
hCrd

```

13. It will ask if you want to exclude any endmembers. Again, we can speed things up by excluding some very uncommon aluminum-free chlorite end-members. First be sure to say "Y" to the prompt asking if you want to exclude any endmembers, then enter these:

```
fafchl_i
mafchl_i
```

14. Everything else should be as in tasks 1-3.

Results

Run VERTEX. It will take a while to run. Instead of a handful of phases whose free energies must be calculated, there are now thousands, because each solution phase is divided into a bunch of pseudocompounds.

Run PSVDRAW as usual to get the plot. Open it in Illustrator. It should look like the figure at right, but with labels on the right for each invariant (not compositionally sensitive) equilibrium reaction. These reactions are marked on the diagram with a black dot. Note, however, that some of them are artifacts created by the discretization algorithm: this makes the curves jagged, and where two touch at a point, there is a false invariant equilibrium created. Those false equilibria (the second, third, and sixth from the top) should be ignored.

Examine the print file. Most of it is made up of a list of the pseudocompounds and their MgO compositions (in mole fraction MgO), but near the end of the file, you will find a list like this:

the stable assemblages at:

```
T(K)      = 773.000
P(bar)    = 7000.00
Y(CO2)    = 0.00000
```

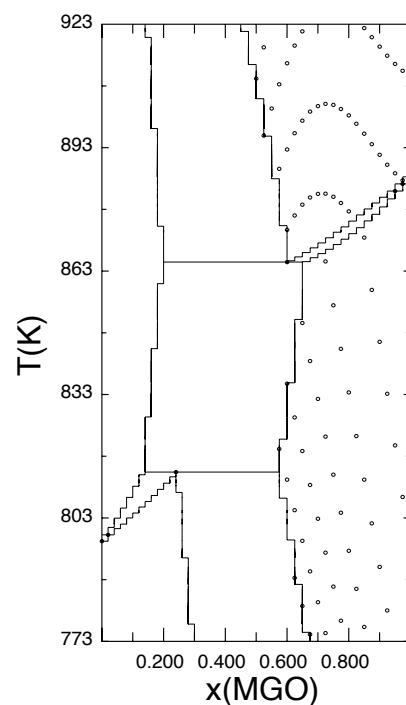
are (variance flag in parentheses):

```
fctd      -fc98.0 (3)    fc98.0 -fc96.0 (3)    fc96.0 -fc94 (3)
fc94      -fc92 (3)      fc92 -fc90 (3)      fc90 -fc88 (3)
fc88      -fc86 (3)      fc86 -fc84 (3)      fc84 -fc82 (3)
fc82      -fc80 (3)      fc80 -fc78 (3)      fc78 -fc76 (3)
fc76      -fc74 (3)      fc74 -fc72 (3)      fc72 -fc70 (3)
fc70      -Ch27_032(1)   Ch27_032-Ch24_030(3) Ch24_030-Ch24_027(3)
Ch24_027-Ch22_024(3)   Ch22_024-Ch22_022(3) Ch22_022-Ch20_020(3)
Ch20_020-Ch20_017(3)   Ch20_017-Ch20_015(3) Ch20_015-Ch17_012(3)
Ch17_012-Ch17_010(3)   Ch17_010-Ch17_0_7(3) Ch17_0_7-Ch15_0_5(3)
Ch15_0_5-Ch15_0_2(3)   Ch15_0_2-Ch15_0_0(3)
```

these assemblages are compatible with the following phases or species determined by component saturation or buffering constraints:

```
q          ky          mu
```

This text tells you the various stable assemblages across the bottom of the plot. It allows you to label the regions along the bottom of the plot. You need to know what the pseudocompound abbreviations mean, though (you can look them up in the file that VERTEX makes called



“pseudocompound_glossary.dat”). In this case, the regions are from low Mg to high Mg: Chloritoid (fctd) on the low-Mg side, Chlorite (Ch) on the high-Mg side, and Ctd + Chl in the middle section, with fixed compositions fc70 and Ch27_032. The reactions listed on the right side of the diagram are those that correspond to the invariant points; these allow you to determine what phases are stable for all the other fields.

For example, the lowest-T reaction (where the two curves coincide on the $X(\text{MgO})=0$ side of the graph) is labeled:

Ctd(HP) (fctd) = St(HP) (fst)

meaning that chloritoid (the iron end-member fctd) reacts directly to staurolite (again, the iron end-member fst). This means that the low-Mg field above that temperature has staurolite stable.

Question 1: What are the stable phases in each field on this T- X_{MgO} plot? Print out the T- X_{MgO} plot, and label each region with the stable phases. Indicate the minerals you are projecting from as well.

Question 2: Look through the print file for the full listing of this reaction (you can find it fairly easily, because it's truly invariant, not pseudoinvariant). Give the full, balanced reaction (but without S and V), and its position in P-T- X_{MgO} space.

Task 6 - Making an AFM diagram

Now that we have some exposure to solid solutions, we'll try something a little more ambitious: the AFM diagram. The reason this is challenging is that Perplex cannot truly plot components below the FeO-MgO join, so we have to “trick” it by changing the system components from FeO and MgO to $\text{Fe}_{0.75}\text{Al}_{-0.25}$ and $\text{Mg}_{0.75}\text{Al}_{-0.25}$. This will allow biotite to plot inside the new, larger triangle.

Building the run file

1. Choose a different name than last time, perhaps “task6.txt”
2. This time, we'll say yes to transform the components. We need to transform three components. The first is K_2O , which we'll replace with $0.5\text{K}_2\text{O} + 1.5\text{Al}_2\text{O}_3$. This is the formula for muscovite (after projecting from water and quartz). This will be one of our components. This step is just the regular projection from muscovite. Here is the interaction:

The current data base components are:

```
NA2O  MGO  AL2O3  SiO2  K2O   CAO   TiO2  MNO   FEO   NIO   ZRO2  CL2
O2     H2O   CO2
```

Transform them (Y/N)?

Y

Enter new component name, < 6 characters, left justified:

KprMs (this can be whatever you want other than a regular oxide name)

Enter old component to be replaced with KprMs:

K2O

Enter other components (< 14) in K 1 per line, <cr> to finish:

AL2O3

Enter stoichiometric coefficients of:

```
K2O  AL2O3
```

in KprMs (in above order):

0.5 1.5

```
KprMs = 0.50 K2O 1.50 AL2O3
```

Is this correct (Y/N)?

Y

3. We'll also do the trick described in the intro paragraph in order to plot biotite correctly. We'll replace FeO with $0.75\text{FeO} - 0.25\text{Al}_2\text{O}_3$, and MgO with $0.75\text{MgO} - 0.25\text{Al}_2\text{O}_3$ (Note that those are real minus signs).
4. Perform the calculations with a saturated **H₂O-only** fluid phase.
5. Also assume that quartz and muscovite are present, and thus require saturated SiO₂, and "K" (the transformed muscovite component).
6. When you choose thermodynamic components, you should choose "FeAFM" (or whatever you called the transformed FeO), "MgAFM" (the transformed MgO), and Al₂O₃. The order you enter those determines which components are on which vertices of the triangle, so they must be entered in that order.
7. This type of diagram is a composition diagram; there are no independent variables.
8. Perform the calculations at 5000 kbar, and every 20 degrees from 500°C to 600°C.
9. Choose to treat solution phases, and use the solution models given in task 5
10. Everything else should be as in tasks 1 & 5.

Results

Run VERTEX. It will take a while to run. When you run PSVDRAW, try doing it first with the tie lines and look at the file that gets produced. Note that the discretization controls the spacing of tie lines. Then redo without tie lines, as the program recommends. Your final output should look like the one at right.

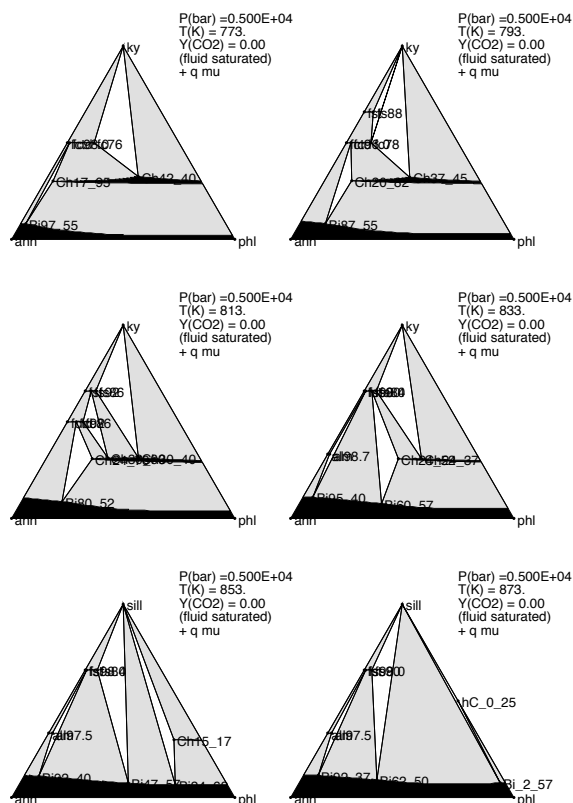
Turn in this plot.

Question 3: Turn in a plot of only the 560°C diagram with all the fields labeled with their stable phases (you may note the projection phases outside the diagram).

Question 4: Describe qualitatively the changes occurring from 773 K through 833 K. If you wanted to get more specific knowledge of these changes, how would you use Perplex to figure those out?

Question 5: Identify the discontinuous reaction(s) that must occur somewhere between 833 and 853 K.

Question 6: Give the exact predicted composition (in terms of end-member proportions) of all minerals stable in this system at 5 kbar, 813 K, and X(CO₂)=0 in a rock whose bulk composition plots in the low-Al 3-phase triangle. You will have to look in the pseudocompound_glossary.dat file for compositions.



Perplex Tutorial 4: Pseudosections

You will recall that a pseudosection is a diagram showing the position of the various reactions in (generally) P–T space, customized for a particular bulk composition. These are very useful for a kind of rough thermobarometry. Note that there is an exhaustive tutorial on pseudosections on the Perplex website: http://www.perplex.ethz.ch/perplex_pseudosection.html

Task 7 - Mineral stability calculation for a pelite.

Here we will calculate the expected mineral stability for a pelite from the sillimanite zone of the Waterville formation in Maine. At right are data from an XRF analysis, in weight percent. These do not sum to 100%; the remainder is presumably H₂O and CO₂.

A full-blown pseudosection can take a very long time (days) to calculate. We'll start by calculating the stable phases at a particular P&T, somewhat like we did in task 1. Note that this is not a pseudosection, but it sets the stage for calculating one. We will assume that quartz is present, along with water-rich fluid.

Building the run file

1. Choose a different name than last time, perhaps "task7.txt"
2. This time, perform the calculations with a saturated H₂O–CO₂ fluid phase, with the composition $X(\text{CO}_2)=0.1$.
3. Assume that quartz is present throughout, and thus requires saturated SiO₂.
4. The thermodynamic components should be all the non-SiO₂ oxides in the above list; order is irrelevant.
5. Choose unconstrained minimization, and then zero for the number of independent potential variables (we are going to choose a fixed value for P&T).
6. It asks now if we want to constrain the bulk composition, which in this case we do.
7. Say yes to each component, and then agree to specify by weight (you can also specify by moles).
8. Enter the amounts listed in the table for the various components.
9. You do want a print file, and you do want to print pseudodivariant assemblage data.
10. You need not bother with a plot file, because the diagram won't be ternary, and so it cannot be plotted.
11. It asks if you want to exclude phases. The whole excluding of phases makes the calculations speedier. In general, you should start by not excluding any phases, and if you get some weird phases forming, then exclude those. Only after you know what phases to consider should you exclude the others. In order to give you a head start, There is a list of phases to exclude in the text file `excluded_phases.txt`. It is quickest to not be prompted, but just to type them in. You could decline to exclude phases for now, but then paste the list into the task7.txt file after BUILD is complete.
12. There is also a list of solution models for you (`soln_models.txt`).
13. Don't forget to also exclude the aluminum-free chlorite end-members.
14. You should perform the calculation at 3.5 kbar, 700 °C, and $X_{\text{CO}_2}=0.1$.
15. Everything else should be as in tasks 1–3.

Results

Run VERTEX. It should take 10–20 seconds to run. There is nothing that can be plotted for these conditions, but you can examine the print file to see what phases are stable.

Question 1. What phases are stable for this bulk composition at these conditions? You will need to mathematically combine the pseudocompounds for each phase into a single phase composition, using the molar percents of each pseudocompound.

Task 8 - P-T Pseudosection

Well, now you've got some idea of what to expect for this rock at its peak conditions, but what about its history? That's where the pseudosection comes in handy. Let's say you were interested in finding out at what temperature garnet began to grow in this rock, and how much grew over time, or perhaps the order of mineral formation. Perhaps you are interested in how things might be different if the fluid composition changed. All these questions can be answered with pseudosections.

Building the run file

1. Choose a different name than last time, perhaps "task8.txt"
2. Everything should be the same as task 7, except the following:
3. Use computational mode 2 (gridded minimization).
4. Calculate a P–T diagram over the range: 2–5 kbar, 200–800°C, and $X(\text{CO}_2)=0.1$. Make pressure the y-axis variable and temperature the x-axis variable.
5. Accept the defaults for the grid refinement mode.
6. To make a fast and rough calculation, set ILOW and JLOW to 20, and set JLEV=2.
7. Do constrain the saturated component, SiO_2 .
8. Make a print file and a plot file.

Results

Run VERTEX. It should take **about 15–30 minutes** to run. Run PSVDRAW to see the plot. It's pretty ugly. You can try to ungroup the objects in Illustrator and drag the text off to the side to read it. One reason it's so ugly is the the coarse resolution of the calculation makes a bunch of tiny, fake fields with different assemblages. If you increase the values of ILOW, JLOW, and JLEV (to 40, 40, and 4), you will get a prettier plot, at the expense of calculation time.

For the rest of this assignment, you should run the quick versions in class, and then redo them at higher quality later, and turn in these higher-quality versions. You can easily change the variables above in the build file (ILOW, JLOW, JLEV) without re-running BUILD. Also, remember that you can easily run perplex on your home computer by downloading it from the website.

Question 2. Draw on the pseudosection the line that separates garnet-bearing rocks from non-garnet-bearing rocks. (Note that some of the tiny regions are artifacts of the coarse resolution of the calculations.) Turn this in.

PSVDRAW has great features that allow us to see very clearly where the garnet-bearing fields are. First make a duplicate of the postscript file that you just made, and name the duplicate something like "task8plotB.txt.ps". Now run PSVDRAW again, and when it asks you if you want to modify the default plot, say yes:

Modify the default plot (y/n)?

y

Modify default drafting options (y/n)?

answer yes to modify:

- picture transformation
- x-y plotting limits
- relative lengths of axes
- text label font size
- line thickness
- curve smoothing
- axes labeling and gridding

n

Restrict phase fields by phase identities (y/n)?

answer yes to:

- show fields that contain a specific assemblage
- show fields that do not contain specified phases
- show fields that contain any of a set of specified phases

y

WARNING: You can not specify saturated phases or phases determined by component saturation constraints in these restrictions.

Show only with assemblage (y/n)?

y

Enter the name of a phase present in the fields
(left justified, <cr> to finish):

Gt (HP)

Enter the name of a phase present in the fields
(left justified, <cr> to finish):

Show only without phases (y/n)?

n

Show only with phases (y/n)?

n

Modify default equilibrium labeling (y/n)?

answer yes to:

- modify/suppress [pseudo-] high variance field labels

n

Change default phase field fill patterns (y/n)?

answer yes to:

- suppress default variance-based phase field patterns
- generate fills based on the value of a property

n

859fields have the assemblage: Gt (HP)

Examine the new plot.

Question 3. Turn this in, indicating at what pressure the garnet-forming reaction is found at the highest temperature. Be sure to give this plot an informative title, as well as the next two.

You can also calculate how much garnet has formed at any given condition. Make another copy of the postscript file, and run PSVDRAW again, modifying the default options, and saying no to all the prompts until it asks about the field fill patterns:

```
Change default phase field fill patterns (y/n)?
answer yes to:
- suppress default variance-based phase field patterns
- generate fills based on the value of a property
```

y

```
Suppress phase field fills (y/n)?
```

n

```
Select a property:
```

- 1 - Specific Enthalpy (J/m3)
- 2 - Density (kg/m3)
- 3 - Specific heat capacity (J/K/m3)
- 4 - Expansivity (1/K, for volume)
- 5 - Compressibility (1/bar, for volume)
- 6 - Weight (%) of a component
- 7 - Mode (Vol, Mol, or Wt proportion) of a phase
- 8 - Composition (Mol or Wt) of a solution
- 9 - Grueneisen thermal ratio
- 10 - Adiabatic bulk modulus (bar)
- 11 - Adiabatic shear modulus (bar)
- 12 - Sound velocity (km/s)
- 13 - P-wave velocity (Vp, km/s)
- 14 - S-wave velocity (Vs, km/s)
- 15 - Vp/Vs
- 16 - Specific entropy (J/K/m3)
- 17 - Entropy (J/K/kg)
- 18 - Enthalpy (J/kg)
- 19 - Heat Capacity (J/K/kg)
- 20 - Specific mass of a phase (kg/m3-solid)
- 21 - Poisson ratio
- 22 - Molar Volume (J/bar)

7

```
Enter solution or compound name (left justified):
```

Gt (HP)

```
Include fluid in computation of aggregate (or modal) properties (y/n)?
```

n

```
**WARNING** at T(K)= 0.000 P(bar)= 0.000 a phase
has invalid physical properties, this may result in
incorrect densities and seismic velocities. this error
can usually be avoided by turning compression off
when you run Vertex (set JTEST=3)
```

[a whole bunch of these warnings appear here]

```
**WARNING** at T(K)= 0.000 P(bar)= 0.000 a phase
has invalid physical properties, this may result in
incorrect densities and seismic velocities. this error
can usually be avoided by turning compression off
when you run Vertex (set JTEST=3)
```

this warning will not be repeated for future

instances of this problem

The property ranges from: 0.00000 -> 16.3182

Enter range (min->max) of the property to be contoured by false color:

0.0 16.3182

Examine the new plot.

Question 4. Turn this in, indicating at what pressure garnet is made the fastest, under isobaric heating (assuming a constant heating rate)?

Finally, you can determine the composition of the garnet being produced. Redo PSVDRAW as above, but this time choose property 8 – the composition of a solution. Here we'll plot the MnO content of the garnet.

1. Choose property 8, and enter the garnet solution model.
2. We'll plot MnO. Select one component in the numerator, MNO (with a weighting value of 1), and give 0 for the denominator (nothing in the denominator).
3. Contour the whole range.

Change default phase field fill patterns (y/n)?

answer yes to:

- suppress default variance-based phase field patterns
- generate fills based on the value of a property

y

Suppress phase field fills (y/n)?

n

Select a property:

- 1 - Specific Enthalpy (J/m3)
- 2 - Density (kg/m3)
- 3 - Specific heat capacity (J/K/m3)
- 4 - Expansivity (1/K, for volume)
- 5 - Compressibility (1/bar, for volume)
- 6 - Weight (%) of a component
- 7 - Mode (Vol, Mol, or Wt proportion) of a phase
- 8 - Composition (Mol or Wt) of a solution
- 9 - Grueneisen thermal ratio
- 10 - Adiabatic bulk modulus (bar)
- 11 - Adiabatic shear modulus (bar)
- 12 - Sound velocity (km/s)
- 13 - P-wave velocity (Vp, km/s)
- 14 - S-wave velocity (Vs, km/s)
- 15 - Vp/Vs
- 16 - Specific entropy (J/K/m3)
- 17 - Entropy (J/K/kg)
- 18 - Enthalpy (J/kg)
- 19 - Heat Capacity (J/K/kg)
- 20 - Specific mass of a phase (kg/m3-solid)
- 21 - Poisson ratio
- 22 - Molar Volume (J/bar)

8

Enter solution or compound name (left justified):

Gt (HP)

Compositions are defined as a ratio of the form:

$$\text{Sum } \{w(i)*n(i), i = 1, c1\} / \text{Sum } \{w(i)*n(i), i = c2, c3\}$$

$n(j)$ = mole proportion of component j
 $w(j)$ = weighting factor of component j (usually 1)

How many components in the numerator of the composition (<16)?

1

Enter component indices and weighting factors for the numerator:

1 - MGO
 2 - AL2O3
 3 - K2O
 4 - CAO
 5 - MNO
 6 - FEO
 7 - SIO2
 8 - H2O
 9 - CO2

5 1

How many components in the denominator of the composition (<15)?

Enter zero to use the numerator as a composition.

0

The compositional variable is: 1.0 MNO

Change it (y/n)?

n

****WARNING**** at T(K)= 0.000 P(bar)= 0.000 a phase
 has invalid physical properties, this may result in
 incorrect densities and seismic velocities. this error
 can usually be avoided by turning compression off
 when you run Vertex (set JTEST=3)

[a whole bunch of these warnings appear here]

****WARNING**** at T(K)= 0.000 P(bar)= 0.000 a phase
 has invalid physical properties, this may result in
 incorrect densities and seismic velocities. this error
 can usually be avoided by turning compression off
 when you run Vertex (set JTEST=3)

this warning will not be repeated for future
 instances of this problem

The property ranges from: 0.000000 ->0.700000

Enter range (min->max) of the property to be contoured by false color:

0 0.6

Examine the new plot.

Question 5. Turn this in, and describe the MnO of the garnet during isobaric heating at 4 kbar. We know that garnet typically has high Mn values in its core and lower values toward the rim. Does that match with what the you would predict from this pseudosection? If not, how can you reconcile the two?

Perplex Assignment

Now that you have learned how to use Perplex, here is your main assignment: You will calculate one or more pseudosections to illustrate some aspect of metamorphic petrology. Here are some ideas:

- You might replicate a calculation you find in a journal article that was performed in Thermocalc, and see how the results differ.
- You might calculate parallel pseudosections for different rock compositions to document the relation between reactions found in each one over some range of reasonable conditions.
- You might learn some other aspect of Perplex (e.g., calculations along a geothermal gradient) and apply it to a model rock or a rock you're working on.
- You might calculate a pseudosection involving a geothermal gradient and apply it to a model rock, or a rock you are working on.

Model bulk compositions for pelites can be found here: Shaw, D. M. (1956) Major elements and general geochemistry, Part 3 of Geochemistry of pelitic rocks, *Geological Society of America Bulletin*, vol.67, no.7, pp.919–934. Other sedimentary and igneous bulk chemical analyses can be found on the web or in journal articles, but here are two easy sources:

- http://minerals.cr.usgs.gov/geo_chem_stand/
- <http://www.aist.go.jp/RIODB/geostand/>

You will give a brief presentation on your results in class.