PERPLE_X TUTORIALS

This set of 13 tutorials has been prepared to teach students how to use Perple_X to make different types of phase diagrams. This is the practical part of a 30 hours advanced course on "Petrologic phase diagrams: principles and computations" periodically offered to PhD students by Daniele Castelli and Chiara Groppo (Dept. of Earth Sciences, University of Torino, Italy).

All the calculations have been performed with **Perple_X version 6.8.6** (released on January 24, 2019). Each tutorial consists of a pdf file with the commented dialogs and a folder containing all the files produced during calculation. The perplex_option.dat file used for each calculation is provided in the corresponding folders.

The exercises should be done **sequentially**, following the order indicated by the numbers. Most of the prompts are, in fact, explained only the first time they appear and comments are not repeated later.

Topics addressed in the 13 exercises are as follows:

Understanding the differences between projections, chemographies and pseudosections

Working with solid solutions

Working with solid solutions in a more complex system

Ex 13: logf(S₂) vs logf(O₂) diagram for the system C-FeO

This exercise explains how to calculate a $\log f(S_2)$ vs. $\log f(O_2)$ pseudosection showing the stability fields of Fe-oxides, Fe-sulphides and graphite as a function of $f(S_2)$ and $f(O_2)$. The exercise is useful to understand how to redefine the thermodynamic components of a database (CTRANSF) and how to deal with fugacities as independent variables.

Ex. 1

Ex. 1 – P-T projection for the Al$_2$SiO$_5$ system

This exercise explains how to calculate a P-T diagram for the very simple, two-components system SiO$_2$-Al$_2$O$_3$ (quartz in excess), showing phase relations among the three alumino-silicate polymorphs.

The influence of different thermodynamic databases on the position of the And-Ky-Sil triple point is also explored.

(1) Definition of the problem (BUILD)

C:\PERPLEX\Perplex686>build

Perple_X version 6.8.6, source updated Jan 24, 2019.
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NO is the default (blank) answer to all Y/N prompts
"default" is what Perple_X assumes if the user simply presses the enter key in response to a prompt.

Enter a name for this project (the name will be used as the root for all output file names) [default = my_project]:
Here you can decide how to name your project.
Project names should not include blanks or "." characters, but they may include directory information. The project name can be up to 100 characters long, but because output files are named using project name plus various suffixes (e.g., .dat, .plt, .prt, .arf, .tof, .tab) it is unwise to specify names that are longer than 93 characters.
ex1
The problem definition file will be named: ex1.dat

Enter thermodynamic data file name [default = hp02ver.dat]:
The thermodynamic data file contains the basic thermodynamic data for all stoichiometric phases and/or species. Typically the files are named XXNNver.dat where XX indicates the authorship or source and NN is the year of the last revision. Sources and brief descriptions of commonly used files are at http://www.perplex.ethz.ch/perplex_thermodynamic_data_file.html.
The HP (Holland & Powell) databases are the most used in metamorphic petrology. One of the most recent HP databases is hp62 (from the THERMOCALC version 6.2; Holland & Powell, 2011). In this exercise we will use the hp02 (Holland & Powell, 1998, revised 2002). We will then compare the results with that obtained using the more recent hp62 database.
hp02ver.dat

Enter the computational option file name [default = perplex_option.dat]:
See: www.perplex.ethz.ch/perplex_options.html
Here you can press RETURN. The perplex_option.dat file specifies some computational parameters that Perple_X uses to make the calculations: **it is better NOT to modify these parameters, at least at the beginning**.

Explanations for each of these parameters are at: http://www.perplex.ethz.ch/perplex_options.html

Reading computational options from: perplex_option.dat
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

This is the lists of the **CHEMICAL COMPONENTS** considered in the chosen database.

This option would permit the user to redefine the database components, e.g., to create Fe2O3 from the components FeO and O2 (i.e. FE2O3 = 2FEO + 0.5 O2).

Component transformations in BUILD are tedious, so if you are going to do many calculations with transformed components the program CTRANSF can be used to create a thermodynamic data file with transformed components.

Specify computational mode:
   1 - Convex-Hull minimization
   2 - Constrained minimization on a 2d grid [default]
   3 - Constrained minimization on a 1d grid
   4 - Output pseudocompound data
   5 - 1-d Phase fractionation calculations
   6 - 0-d Infiltration-reactionation-fractionation
   7 - 2-d Phase fractionation (FRAC2D and TITRATE reactive transport models)
Use Convex-Hull minimization for Schreinemakers projections or phase diagrams with > 2 independent variables. Use constrained minimization for phase diagrams or phase diagram sections with < 3 independent variables.
1

Use option 1 (Convex-Hull minimization) for PROJECTIONS (Schreinemakers-type diagrams) or CHEMOGRAPHIES (composition diagrams; phase diagrams with > 2 independent variables). Use options 2 or 3 (Constrained minimization on a 2d grid/1d grid) for PSEUDOSECTIONS (phase diagrams or phase diagram sections with < 3 independent variables).

Calculations with a saturated   FLUID (Y/N)?
N

Fluid is not considered in this specific calculation, because reactions among alumina-silicates are solid-solid reactions.

Calculations with saturated components (Y/N)?
SATURATED COMPONENTS are components whose chemical potentials are determined by the assumed stability of a pure phase consisting entirely of a saturated component, e.g., a system that contains so much silica that a silica polymorph (e.g., quartz or coesite) is stable at all conditions of interest can be specified here by selecting SiO2 as a saturated component.
NB. If more than one saturated component is specified, Perple_X applies the constraints sequentially, e.g., if Al2O3 and SiO2 are specified as the first and second components, then the excess phases might be corundum + andalusite, if the order is reversed then, at the same conditions, the stable phases would be quartz + andalusite. This sequence is referred to as the saturation hierarchy.
Y

warning ver015 if you select > 1 saturated component, then the order you enter the components determines the saturation heirarchy and may effect your results (see Connolly 1990).

Select < 6 saturated components from the set:
 NA2O MGO AL2O3 SIO2 K2O CAO TIO2 MNO FEO NIO ZRO2 CL2 O2   H2O CO2
Enter names, 1 per line, press <enter> to finish:
SIO2
(NB. It is CASE-SENSITIVE!).

Use chemical potentials, activities or fugacities as independent variables (Y/N)?
N
The answer would be Y if you want to calculate a phase diagram with chemical potentials (μ), activities or fugacities on one (or on both) axes (e.g. T-logfO_2 phase diagrams).

Select thermodynamic components from the set:
NA2O MGO   AL2O3 SIO2 K2O CAO TIO2 MNO FEO NIO ZRO2 CL2 O2   H2O CO2
Enter names, 1 per line, press <enter> to finish:
AL2O3
Here is where you specify the components for your system.
THERMODYNAMIC COMPONENTS are components whose chemical potentials are the dependent (implicit) variables of a phase diagram calculation. **Phase diagram calculations require the specification of at least one thermodynamic component.**

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
The answer would be Y if you want to consider a geothermal gradient along an axes, rather than P or T.

Specify number of independent potential variables:
    0 - Composition diagram [default]
    1 - Mixed-variable diagram
    2 - Sections and Schreinemakers-type diagrams
2
0 = chemografies (*see Ex3*);
1 = T-X or P-X diagrams (e.g. T-XMgO)
2= classical phase diagram projections and sections
See the comment above.

Select x-axis variable:
    1 - P(bar)
    2 - T(K)
2

Enter minimum and maximum values, respectively, for: T(K)
473
1073
T is expressed in Kelvin

Enter minimum and maximum values, respectively, for: P(bar)

1000

12000

P is expressed in bar

Output a print file (Y/N)?

Y

Exclude pure and/or endmember phases (Y/N)?

N

Here you can specify if you want to exclude some phases from the calculation.

Include solution phases (Y/N)?

N

Solid solutions are not considered, because we are modelling reactions between end-member phases.

Enter calculation title:

ex1

This name appears at the top of the diagram.

After finishing with BUILD, a .dat file is generated within the Perple_X folder. This new file (named ex1.dat) is the input file for the following calculation steps.

(2) Doing the calculation (CONVEX)

Run CONVEX to make the calculation:

C:\Perplex\Perplex686>convex

Perple_X version 6.8.6, source updated Jan 24, 2019.
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Enter the project name (the name assigned in BUILD) [default = my_project]:
ex1

This section summarizes where CONVEX reads the input data (thermodynamic database, input file generated with build etc.), and where CONVEX writes the results (print output, plot output).
Reading thermodynamic data from file: hp02ver.dat
Reading solution models from file: not requested
Writing print output to file: EX1.prn
Writing plot output to file: EX1.plt
Reading Perple_X options from: perplex_option.dat
Writing complete reaction list to file: not requested
Writing Perple_X option summary to file: not requested

Perple_X version 6.8.5, source updated Dec 20, 2018.
Copyright (C) 1986-2018 James A D Connolly <www.perplex.ethz/copyright.html>.

This section summarizes all the parameters ("computational option settings") used in the calculation and specified in the perplex_option.dat file.
Perple_X computational option settings for CONVEX:
    Keyword: Value: Permitted values [default]:
 Auto-refine options:
  auto_refine   man   off manual [auto]
 Schreinemakers and Mixed-variable diagram options:
  variance   1 /99   [1/99], >0, maximum true variance
  increment   0.100/0.025 [0.1/0.025], default search/trace variable increment
  efficiency   3   [3] >0 < 6
  reaction_format   min   [min] full stoichiometry S+V everything
  reaction_list   off   [off] on
  console_messages   on   [on] off
  short_print_file   on   [on] off
 Solution subdivision options:
  initial_resolution:
   exploratory stage   0.0625   0->1 [1/16], 0 => off
   auto-refine stage   0.0208   0->1 [1/48], 0 => off
  stretch_factor   0.0020   >0 [2d-3]
  subdivision_override off   [off] lin str
  hard_limits   off   [off] on
  refine_endmembers   F   [F] T
  pc_perturbation   0.0050   [5d-3]
 Thermodynamic options:

solvus_tolerance   aut   [aut] or 0->1; aut = automatic, 0 => p=c pseudocompounds, 1 => homogenize
T_stop (K)   0.0   [0]
T_melt (K)   873.0   [873]
order_check   on   off [on]
approx_alpha   T   [T] F
Anderson-Gruneisen   F   [F] T
speciation_factor   100.   >10 [100] speciation precision = final resolution/speciation_factor
speciation_max_it   100   [100]
hybrid_EoS_H2O   4   [4] 0-2, 4-7
hybrid_EoS_CO2   4   [4] 0-4, 7
hybrid_EoS_CH4   0   [0] 0-1, 7
aq_bad_results   err   [err] 101, 102, 103, ignore
aq_lagged_speciation F   [F] T
aq_ion_H+   T   [T] F => use OH-
aq_oxide_components   F   [F] T
aq_solvent_solvus   T   [T] F
aq_vapor_epsilon   1.0   [1.]
Input/Output options:
dependent_potentials off   off [on]
pause_on_error   T   [T] F
auto_exclude   T   [T] F
Worst case (Cartesian) compositional resolution (mol):
Exploratory stage: 0.833E-2
Auto-refine stage: 0.651E-3
Adapative minimization will be done with:
  4 iterations in the exploratory stage
  5 iterations in the autorefine stage
To change these options see: www.perplex.ethz.ch/perplex_options.html

Summary of make-definition entities:
sil8L   q8L

This is the calculation.
** Starting auto_refine computational stage **
Testing divariant assemblage   1,   0 assemblages remaining to be tested.
finished with equilibrium (1) ky = and
finished with equilibrium (2) ky = sill
finished with equilibrium (3) and = sill
Testing divariant assemblage   2,   0 assemblages remaining to be tested.
Testing divariant assemblage   3,   0 assemblages remaining to be tested.
Testing divariant assemblage   4,   0 assemblages remaining to be tested.

At the end, you have two new files in the Perple_X folder. An ex1.prn file, which is the text file with all the information about the calculation, and an ex1.plt file, that is the plot file.

(3a) Plotting the calculated phase diagram (PSVDRAW)

Run PSVDRAW to plot the calculated phase diagram:

C:\PERPLEX\Perplex686>psvdraw

Perple_X version 6.8.6, source updated Jan 24, 2019.
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Enter the project or plot file name [i.e., without the .plt suffix]:
ex1

Perple_X plot options are currently set as:
```
   Keyword:          Value:    Permitted values [default]:
   axis_label_scale     1.20      [1.2] (rel)
   bounding_box :
                    0     [0] x-min (pts)
                    0     [0] y-min (pts)
                  800     [800] x-length (pts)
                  800     [800] y-length (pts)
   field_fill        T        [T] F
   field_label       T        [T] F
   field_label_scale    0.75      [0.72] (rel)
   font              Helvetica
   grid              F        [F] T
   half_ticks        T        [T] F
   line_width          1.00      0-99 [1.] (pts)
   picture_transformation :
                  0.180    [0.18] x-scale (rel)
                  0.180    [0.18] y-scale (rel)
                   130.    [0.18] x-translation (pts)
                   220.    [0.18] y-translation (pts)
                  0.00    [0.0]  rotation (deg)
   plot_aspect_ratio    1.000    [1.0] x_axis_length/y_axis_length
   replicate_label      0.250    0->1 [0.025]
   splines           T        [T] F
   tenth_ticks       F        [F] T
   text_scale          1.000    [1.] (rel)
```
To change these options edit or create the plot option file See: www.perplex.ethz.ch/perplex_plot_options.html

PostScript will be written to file: ex1.ps

Modify the default plot (y/n)?
N
If you replay Y to this prompt, you can change the output, for example you can modify the minimum and maximum T or P along the axes etc. (see below).
At the end, you have a new file ex1.ps in the Perple_X folder. You can open this file with any graphical software (e.g. CorelDraw, Adobe Illustrator etc.) and also convert it in a pdf file.

ex1
Component saturation hierarchy: SIO2
Reaction equations are written with the high T(K) assemblage to the right of the = sign
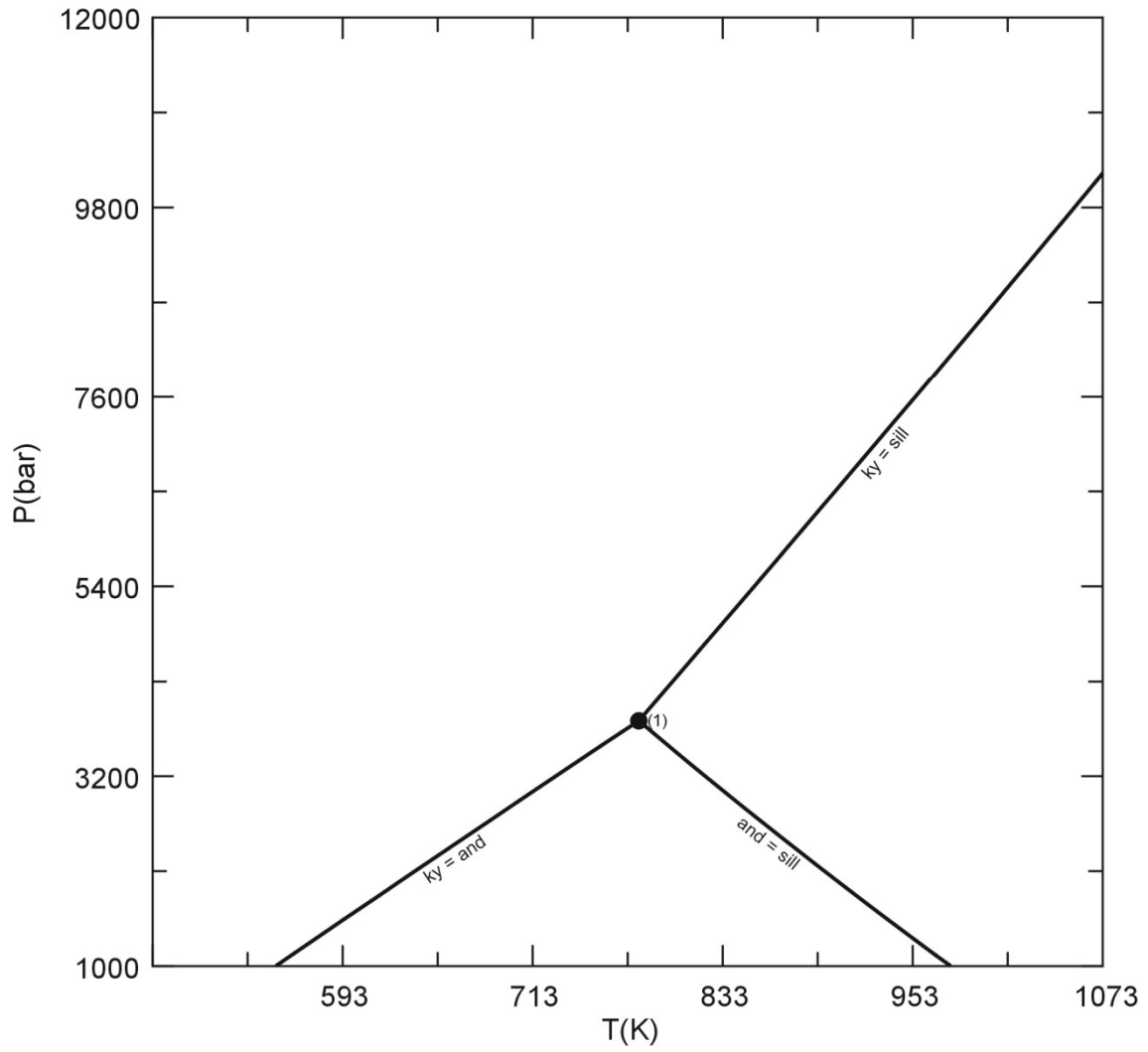
The alumino-silicate triple point is modelled at 507°C, 3.8 kbar.

(3b) Modifying the default plotting of the calculated phase diagram (PSVDRAW)

E.g. we want to modify the axes numbering (intervals on x axis = 100°C; intervals on y axis = 2 kbar) and we want to assign a numeric label (rather than a text label) to the reaction curves.

Run again PSVDRAW:

C:\PERPLEX\Perplex686>psvdraw

Perple_X version 6.8.6, source updated Jan 24, 2019.
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Enter the project or plot file name [i.e., without the .plt suffix]:
ex1

Perple_X plot options are currently set as:
```
  Keyword:        Value:    Permitted values [default]:
  axis_label_scale    1.20      [1.2] (rel)
  bounding_box :
                0     [0] x-min (pts)
                0     [0] y-min (pts)
              800    [800] x-length (pts)
              800    [800] y-length (pts)
  field_fill       T      [T] F
  field_label      T      [T] F
  field_label_scale   0.75    [0.72] (rel)
  font          Helvetica
  grid          F      [F] T
  half_ticks       T      [T] F
  line_width       1.00     0-99 [1.] (pts)
  picture_transformation :
              0.180    [0.18] x-scale (rel)
              0.180    [0.18] y-scale (rel)
               130.    [0.18] x-translation (pts)
               220.    [0.18] y-translation (pts)
              0.00     [0.0]  rotation (deg)
  plot_aspect_ratio    1.000    [1.0] x_axis_length/y_axis_length
  replicate_label     0. 250     0->1 [0.025]
  splines        T      [T] F
  tenth_ticks      F      [F] T
  text_scale       1.000    [1.] (rel)
```
To change these options edit or create the plot option file See: www.perplex.ethz.ch/perplex_plot_options.html

PostScript will be written to file: ex1.ps

Modify the default plot (y/n)?
y

Modify drafting options (y/n)?
 answer yes to modify:

- x-y plotting limits
- axes numbering

y

Modify x-y limits (y/n)?

Answer Y if you want to modify the T and/or P range of the diagram.

n

Restrict phase fields by variance (y/n)?
  answer yes to:
  - suppress pseudounivariant curves and/or pseudoinvariant points of a specified true variance.

This question is only relevant for more complex calculations, involving solution models and therefore considering also pseudo-univariant curves (i.e. di-variant equilibria involving two pseudocompounds of the same phase as reactant and product). *See Ex. 7*.

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

n

Modify default equilibrium labeling (y/n)?
  answer yes to:
  - modify/suppress [pseudo-] univariant curve labels
  - suppress [pseudo-] invariant point labels

y

Suppress curve labels (y/n)?

n

Change default labeling of curve segments (y/n)?

y

Suppress labels of pseudounivariant curves (y/n)?

y

Enter minimum fraction of the axes length that a curve must be to receive a text label (0-1):

1 means that a text label will be assigned to those curves that are longer than the axes length.

1

Enter minimum fraction of the axes length that a curve must be to receive a numeric label (0-1.000):

0 means that a numeric label will be assigned to all those curves that are shorter than the axes length.

0

Suppress point labels (y/n)?

n

Modify default axes numbering (y/n)?

Enter the starting value and interval for major tick marks on the X-axis (current values are: 473.   160.   )
Enter the new values:

473
100

Enter the starting value and interval for major tick marks on the Y-axis (current values are: 500. 0.390E+04)
Enter the new values:

1000
2000

Equilibria corresponding to each reaction number are explained in the ex1.prn file.

(4) Using a different thermodynamic database

In order to test the influence of different thermodynamic databases on the position of the And-Ky-Sil triple point, you can edit the input file previously created using BUILD.

Open the **ex1.dat** input file and change its name in **ex1_hp62.dat**

The thermodynamic database is specified in the first line.
Change **hp02ver.data** in **hp62ver.dat**.

hp62ver.dat   thermodynamic data file

The most recent databases such as hp62ver.dat, define thermodynamic components with both upper and lower case characters (e.g. SiO2, Al2O3 etc.), opposite to the old databases, in which thermodynamic components were defined with upper case characters only (e.g. SIO2, AL2O3 etc.).
In the input file, change the thermodynamic components accordingly.

begin thermodynamic component list
Al2O3 0 0.00000   0.00000   0.00000   unconstrained amount
end thermodynamic component list

begin saturated component list
SiO2 0 0.00000   0.00000   0.00000   unconstrained amount
end saturated component list

Run again CONVEX and PSVDRAW and compare the result with that previously obtained.
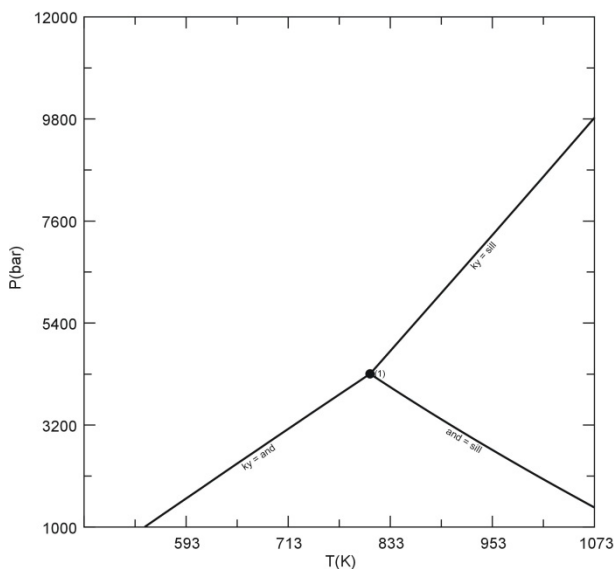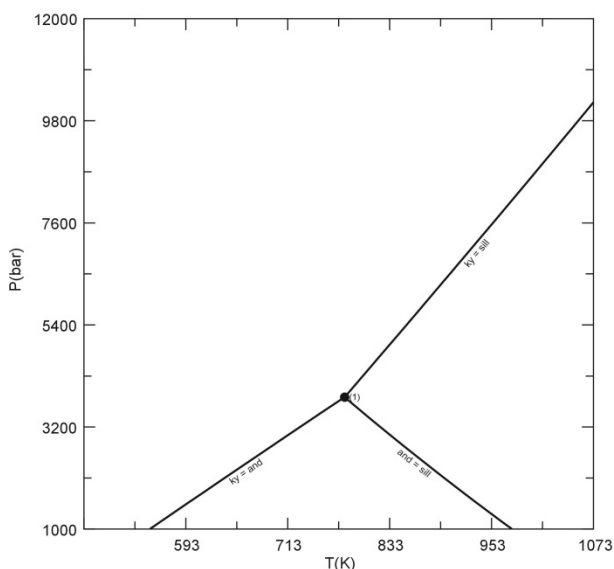
The alumino-silicate triple point is now modelled at 550°C, 4.4 kbar.
The change in the position of the triple point dates back to the 2004 revision of the HP database. In the 2002 version (hp02ver.dat) the aluminosilicate triple point is at 3.8 kbar and 507 °C, consistent with Holdaway's (1971) estimate; in the 2004 revision (and in the following versions, such as hp62ver.dat) the properties of the aluminosilicates have been adjusted to place the triple point at 4.4 kbar and 550 °C to satisfy a petrological argument of Pattison (1992).

Ex. 2

Ex. 2 – P-T projection for the CMSH system (<u>no solid solutions</u>)

This exercise explains how to calculate a P-T projection for the very simple CMSH system; the grid will show all the possible equilibria for this system in the P-T range 200-1000°C, 0.5-20 kbar.

(1) Definition of the problem (BUILD)

C:\PERPLEX\Perplex686>build

Perple_X version 6.8.6, source updated Jan 24, 2019.
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NO is the default (blank) answer to all Y/N prompts

Enter a name for this project (the name will be used as the root for all output file names) [default = my_project]:
Ex2
The problem definition file will be named: ex2.dat

Enter thermodynamic data file name [default = hp02ver.dat]:
The HP (Holland & Powell) databases are the most used in metamorphic petrology. One of the most recent HP databases is hp62 (from the THERMOCALC version 6.2; Holland & Powell, 2011). I suggest using the hp62ver.dat database, which has been tested in the last years and has demonstrated to be reliable.
hp62ver.dat

Enter the computational option file name [default = perplex_option.dat]:
See: www.perplex.ethz.ch/perplex_options.html
[RETURN]

Reading computational options from: perplex_option.dat

The current data base components are:
Na2O MgO Al2O3 SiO2 K2O CaO TiO2 MnO FeO NiO ZrO2 Cl2 O2   H2O CO2 CuO Cr2O3 S2   F2
Transform them (Y/N)?
N
This is the lists of the **CHEMICAL COMPONENTS** considered in the chosen database.
This option would permit the user to redefine the database components, e.g., to create Fe2O3 from the components FeO and O2 (i.e. FE2O3 = 2FEO + 0.5 O2).
Component transformations in BUILD are tedious, so if you are going to do many calculations with transformed components the program CTRANSF can be used to create a thermodynamic data file with transformed components.

Specify computational mode:
    1 - Convex-Hull minimization
    2 - Constrained minimization on a 2d grid [default]

3 - Constrained minimization on a 1d grid

4 - Output pseudocompound data

5 - 1-d Phase fractionation calculations

6 - 0-d Infiltration-reactionation-fractionation

7 - 2-d Phase fractionation (FRAC2D and TITRATE reactive transport models)

Use Convex-Hull minimization for Schreinemakers projections or phase diagrams with > 2 independent variables. Use constrained minimization for phase diagrams or phase diagram sections with < 3 independent variables.

1

Use option 1 (Convex-Hull minimization) for PROJECTIONS (Schreinemakers-type diagrams) or CHEMOGRAPHIES (composition diagrams; phase diagrams with > 2 independent variables). Use options 2 or 3 (Constrained minimization on a 2d grid/1d grid) for PSEUDOSECTIONS (phase diagrams or phase diagram sections with < 3 independent variables).

Calculations with a saturated   FLUID (Y/N)?

Y

There are two important implications to specifying a **SATURATED PHASE**: 1) it implies that the phase components are always present in sufficient quantity to saturate the system in the phase; 2) it implies that the specified phase is always stable. Thus, if you are interested in a system with excess H2O, but the physical conditions of the system may be those at which ice is stable, you should specify H2O as a saturated component and not as saturated phase. Similarly, if water may not be always present as a pure phase you should specify H2O as a thermodynamic component.

In most cases, fluid can be considered as in excess. This means that the user should consider a saturated fluid in the calculation (e.g. H_2O, CO_2 or a mixture of H_2O+CO_2).

NOTE: Because specification of H_2O as a saturated phase component causes Perple_X to exclude any phases with the H_2O composition that are not named "H2O", H2O should not be specified as a saturated fluid phase in calculations involving a hydrous silicate melt if, as is commonly the case, the melt model involves a water end-member that is not named "H2O" (e.g. h2oL). This means that, for calculations at supra-solidus conditions (e.g. melt-bearing systems), the user must consider H2O as a normal chemical component, and not as a saturated fluid phase (*see Ex. 11 and Ex. 12*).

Select the independent saturated   FLUID components:

 H2O   CO2

Enter names, 1 per line, press <enter> 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

Calculations with saturated components (Y/N)?

N

SATURATED COMPONENTS are components whose chemical potentials are determined by the assumed stability of a pure phase consisting entirely of a saturated component , e.g., a system that contains so much silica that a silica polymorph (e.g., quartz or coesite) is stable at all conditions of interest can be specified here by selecting SiO2 as a saturated component.

If more than one saturated component is specified Perple_X applies the constraints sequentially, e.g., if Al2O3 and SiO2 are specified as the first and second components, then the excess phases might be corundum + andalusite, if the order is reversed then, at the same conditions, the stable phases would be quartz + andalusite. This sequence is referred to as the saturation hierarchy.

Use chemical potentials, activities or fugacities as independent variables (Y/N)?
N
The answer would be Y if you want to calculate a phase diagram with chemical potentials (μ), activities or fugacities on one (or on both) axes (e.g. T-logfO_2 phase diagrams).

Select thermodynamic components from the set:
Na2O MgO Al2O3 SiO2 K2O CaO TiO2 MnO FeO NiO ZrO2 Cl2 O2   CO2 CuO Cr2O3 S2   F2
Enter names, 1 per line, press <enter> to finish:
MgO
CaO
SiO2

Because the thermodynamic data file identifies: H2O as special components, you will be prompted next for the EoS to be used for the corresponding composants and mixtures thereof. To override this behavior, e.g., to use a generic hybrid fluid EoS, delete the special_component section from the thermodynamic data file header.

Select fluid equation of state:
  0 - X(CO2) H2O-CO2 Modified Redlich-Kwong (MRK) DeSantis et al 74
  1 - X(CO2) H2O-CO2 HSMRK Kerrick & Jacobs 81
  2 - X(CO2) H2O-CO2 MRK hybrid-EoS*
  5 - X(CO2) H2O-CO2 CORK Holland & Powell 91, 98
  8 - f(O2/CO2) C-buffered COH MRK hybrid-EoS*
  10 - X(O) C-buffered COH MRK hybrid-EoS Connolly & Cesare 93*
  12 - X(O)-f(S2) C-buffered COHS MRK hybrid-EoS Connolly & Cesare 93*
  13 - X(H2) H2O-H2 MRK hybrid-EoS*
  14 - X(CO2) H2O-CO2 Pitzer & Sterner 94; Holland & Powell mixing 03
  15 - X(H2) H2O-H2 low T MRK hybrid-EoS*
  16 - X(O) H-O MRK hybrid-EoS*
  17 - X(O)-f(S2) H-O-S MRK hybrid-EoS*
  19 - X(O)-X(S) C-buffered COHS MRK hybrid-EoS Connolly & Cesare 93*
  20 - X(O)-X(C) COHS MRK hybrid-EoS Connolly & Cesare 93*
  24 - f(O2/CO2)-N/C C-buffered COHN MRK hybrid-EoS*
  25 - X(CO2)-X(NaCl) H2O-CO2-NaCl Aranovich et al 10
  26 - X(O) O-Si MRK Connolly 16
  27 - X(O)-X(C) C-O-H MRK hybrid-EoS*
*Hybrid EoS use the following pure species EoS, to change these associations modify the hybrid_EoS keywords in the perplex_option file:
    H2O - PSEoS Pitzer & Sterner 1994
    CO2 - PSEoS Pitzer & Sterner 1994
    CH4 - HSMRK Kerrick & Jacobs 1981
5
Here you define the **EQUATION OF STATE (EoS) for the fluid phase**.
Most thermodynamic databases are based on equilibria which involve a fluid phase, and are therefore derived with a specific fluid equation of state. When using such databases **it is usually wise to choose (if**

possible) the fluid EoS used in the data derivation for calculations. Thus, **the Holland & Powell (1991, 1998) EoS (choice 5) is optimal for the Holland & Powell 's databases;** and Kerrick & Jacobs' (1981) equation of state (choice 1) (or the hybrid equations of state, e.g. choices 2, 8 or 10) for Berman's (1988) database. At high pressures above 20 kbar most of the equations of state for water become thermodynamically unrealistic, CORK (choice 5) minimizes this problem.

For rough calculations the differences between the EoS are not important and **in the interest of saving computer time choices 5 and 0 are optimal**. Choices 12-27 are equations of state for multispecies H-O, H-O-S, C-O-H, C-O-H-S and H2O-CO2-NaCl fluids.

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
The answer would be Y if you want to consider a geothermal gradient along an axes, rather than P or T.

Specify number of independent potential variables:
   0 - Composition diagram [default]
   1 - Mixed-variable diagram
   2 - Sections and Schreinemakers-type diagrams
2
0 = chemografies;
1 = T-X or P-X diagrams (e.g. T-XMgO)
2= classical phase diagram projections and sections
See the comment above.

Select x-axis variable:
   1 - P(bar)
   2 - T(K)
   3 - Y(CO2)
*Although only one component is specified for the Y(CO2) phase, its equation of state permits use of its compositional variable:
2

Enter minimum and maximum values, respectively, for: T(K)
473
1273
T is expressed in Kelvin

Select y-axis variable:
   2 - P(bar)
   3 - Y(CO2)
2

Enter minimum and maximum values, respectively, for: P(bar)
500
20000
P is expressed in bar

Specify sectioning value for: Y(CO2)

0

Output a print file (Y/N)?
Y

For unconstrained minimization calculations, particularly mixed-variable diagrams and Schreinemakers projections, **the print file contains a summary of the computed phase equilibria**.

warning ver051 cannot make hmjL because of missing data or an invalid definition in the thermodynamic data file.
…
…

Exclude pure and/or endmember phases (Y/N)?
Y

Here you can specify if you want to exclude some phases from the calculation, and if you want to see the list of the mineral phases compatible with your system. The end-member phases are identified by abbreviated names, in general these abbreviations are defined in the header section of the thermodynamic data file. Phases followed by L (e.g. qL) are required for the melt solution and you can therefore exclude them for calculations without melt.

Do you want to be prompted for phases (Y/N)?
N

Enter names, 1 per line, press <enter> to finish:
I suggest excluding the following end-member phases, which are not relevant for this calculation.
cumm_dqf
fo8L
q8L
cenjh
odi
qjL
dijL
fojL
foTL
mcpv
cmpv
foHL
qHL
ak
chum
lrn
merw
mont
rnk
cen
cpv
cstn

cumm
wo
pswo
wal
woL
limL

Include solution phases (Y/N)?
N
Solid solutions are not considered in this case, because we are modelling reactions between end-member phases.

Enter calculation title:
Ex2

(2) Doing the calculation (CONVEX)

Run CONVEX to make the calculation:

C:\Perplex\Perplex686>convex

Perple_X version 6.8.6, source updated Jan 24, 2019.
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Enter the project name (the name assigned in BUILD) [default = my_project]:
Ex2

Reading thermodynamic data from file: hp62ver.dat
Reading solution models from file: not requested
Writing print output to file: EX2.prn
Writing plot output to file: EX2.plt
Reading Perple_X options from: perplex_option.dat
Writing complete reaction list to file: not requested
Writing Perple_X option summary to file: not requested

Perple_X version 6.8.6, source updated Jan 24, 2019.
Copyright (C) 1986-2019 James A D Connolly <www.perplex.ethz/copyright.html>.

Perple_X computational option settings for CONVEX:
  Keyword: Value: Permitted values [default]:
 Auto-refine options:
   auto_refine   man   off manual [auto]
 Schreinemakers and Mixed-variable diagram options:
   variance   1 /99   [1/99], >0, maximum true variance
   increment   0.100/0.025 [0.1/0.025], default search/trace variable increment
   efficiency   3   [3] >0 < 6
   reaction_format   min   [min] full stoichiometry S+V everything
   reaction_list   off   [off] on
   console_messages   on   [on] off

short_print_file   on   [on] off
  Solution subdivision options:
   initial_resolution:
     exploratory stage   0.0625   0->1 [1/16], 0 => off
     auto-refine stage   0.0208   0->1 [1/48], 0 => off
   stretch_factor   0.0020   >0 [2d-3]
   subdivision_override   off   [off] lin str
   hard_limits   off   [off] on
   refine_endmembers   F   [F] T
   pc_perturbation   0.0050   [5d-3]
  Thermodynamic options:
   solvus_tolerance   aut   [aut] or 0->1; aut = automatic, 0 => p=c pseudocompounds, 1 => homogenize
   T_stop (K)   0.0   [0]
   T_melt (K)   873.0   [873]
   order_check   on   off [on]
   approx_alpha   T   [T] F
   Anderson-Gruneisen   F   [F] T
   speciation_factor   100.   >10 [100] speciation precision = final resolution/speciation_factor
   speciation_max_it   100   [100]
   hybrid_EoS_H2O   4   [4] 0-2, 4-7
   hybrid_EoS_CO2   4   [4] 0-4, 7
   hybrid_EoS_CH4   0   [0] 0-1, 7
   aq_bad_results   err   [err] 101, 102, 103, ignore
   aq_lagged_speciation F   [F] T
   aq_ion_H+   T   [T] F => use OH-
   aq_oxide_components   F   [F] T
   aq_solvent_solvus   T   [T] F
   aq_vapor_epsilon   1.0   [1.]
  Input/Output options:
   dependent_potentials   off   off [on]
   pause_on_error   T   [T] F
   auto_exclude   T   [T] F
  Worst case (Cartesian) compositional resolution (mol):
   Exploratory stage: 0.521E-2
   Auto-refine stage: 0.868E-3
  Adapative minimization will be done with:
   4 iterations in the exploratory stage
   5 iterations in the autorefine stage
To change these options see: www.perplex.ethz.ch/perplex_options.html

warning ver051 cannot make hmjL because of missing data or an invalid definition in the thermodynamic data file
…

This is the calculation.
** Starting auto_refine computational stage **
 cycle   1   1   1
 cycle   2   2   3
 cycle   3   4   5
 cycle   4   6   7
Initial number of divariant assemblages to be tested is: 7
Testing divariant assemblage   1,   6 assemblages remaining to be tested.

finished with equilibrium (1) br = per
Testing divariant assemblage   2,   6 assemblages remaining to be tested.
finished with equilibrium (2) q = trd
Testing divariant assemblage   3,   6 assemblages remaining to be tested.
finished with equilibrium (3) br atg = fo
finished with equilibrium (4) liz = br atg
Testing divariant assemblage   4,   9 assemblages remaining to be tested.
finished with equilibrium (5) tr = di q en
finished with equilibrium (6) di ta = tr
Testing divariant assemblage   5,   10 assemblages remaining to be tested.
finished with equilibrium (7) di atg = tr fo
Testing divariant assemblage   6,   12 assemblages remaining to be tested.
finished with equilibrium (8) ta = q anth
finished with equilibrium (9) ta = q en
finished with equilibrium (10) anth = q en
finished with equilibrium (11) ta en = anth
finished with equilibrium (12) ta fo = anth
finished with equilibrium (13) ta fo = en
finished with equilibrium (14) anth fo = en
finished with equilibrium (15) ta atg = en
finished with equilibrium (16) atg = ta fo
finished with equilibrium (17) atg = en fo
Testing divariant assemblage   7,   12 assemblages remaining to be tested.
finished with equilibrium (16) atg = ta fo
Testing divariant assemblage   8,   12 assemblages remaining to be tested.
Testing divariant assemblage   9,   12 assemblages remaining to be tested.
Testing divariant assemblage   10,   12 assemblages remaining to be tested.
Testing divariant assemblage   11,   11 assemblages remaining to be tested.
Testing divariant assemblage   12,   11 assemblages remaining to be tested.
Testing divariant assemblage   13,   11 assemblages remaining to be tested.
Testing divariant assemblage   14,   11 assemblages remaining to be tested.
Testing divariant assemblage   15,   11 assemblages remaining to be tested.
Testing divariant assemblage   16,   12 assemblages remaining to be tested.
Testing divariant assemblage   17,   11 assemblages remaining to be tested.
finished with equilibrium (18) tr fo = di en
Testing divariant assemblage   18,   14 assemblages remaining to be tested.
Testing divariant assemblage   19,   15 assemblages remaining to be tested.
Testing divariant assemblage   20,   15 assemblages remaining to be tested.
Testing divariant assemblage   21,   16 assemblages remaining to be tested.
Testing divariant assemblage   22,   15 assemblages remaining to be tested.
Testing divariant assemblage   23,   14 assemblages remaining to be tested.
Testing divariant assemblage   24,   14 assemblages remaining to be tested.
Testing divariant assemblage   25,   13 assemblages remaining to be tested.
Testing divariant assemblage   26,   12 assemblages remaining to be tested.
Testing divariant assemblage   27,   12 assemblages remaining to be tested.
Testing divariant assemblage   28,   11 assemblages remaining to be tested.
Testing divariant assemblage   29,   10 assemblages remaining to be tested.
Testing divariant assemblage   30,   10 assemblages remaining to be tested.
Testing divariant assemblage   31,   9 assemblages remaining to be tested.
Testing divariant assemblage   32,   8 assemblages remaining to be tested.
Testing divariant assemblage   33,   8 assemblages remaining to be tested.

Testing divariant assemblage   34,   7 assemblages remaining to be tested.
Testing divariant assemblage   35,   6 assemblages remaining to be tested.
Testing divariant assemblage   36,   5 assemblages remaining to be tested.
Testing divariant assemblage   37,   5 assemblages remaining to be tested.
Testing divariant assemblage   38,   4 assemblages remaining to be tested.
Testing divariant assemblage   39,   3 assemblages remaining to be tested.
Testing divariant assemblage   40,   4 assemblages remaining to be tested.
Testing divariant assemblage   41,   5 assemblages remaining to be tested.
Testing divariant assemblage   42,   6 assemblages remaining to be tested.
Testing divariant assemblage   43,   5 assemblages remaining to be tested.
Testing divariant assemblage   44,   5 assemblages remaining to be tested.
Testing divariant assemblage   45,   4 assemblages remaining to be tested.
warning ver066 Metastable assemblage into FLIPIT:
    tr   atg   en
v = 20000.0   888.000   0.00000   0.00000   0.00000
Testing divariant assemblage   46,   3 assemblages remaining to be tested.
warning ver066 Metastable assemblage into FLIPIT:
    tr   atg   fo
v = 20000.0   888.000   0.00000   0.00000   0.00000
Testing divariant assemblage   47,   2 assemblages remaining to be tested.
Testing divariant assemblage   48,   1 assemblages remaining to be tested.
Testing divariant assemblage   49,   0 assemblages remaining to be tested.
Testing divariant assemblage   50,   0 assemblages remaining to be tested.

(3a) Plotting the calculated phase diagram (PSVDRAW)

Run PSVDRAW to plot the calculated phase diagram:

C:\PERPLEX\Perplex686>psvdraw

Perple_X version 6.8.6, source updated Jan 24, 2019.
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Enter the project or plot file name [i.e., without the .plt suffix]:
Ex2

Perple_X plot options are currently set as:
    Keyword: Value: Permitted values [default]:
    axis_label_scale   1.20   [1.2] (rel)
    bounding_box :
                0   [0] x-min (pts)
                0   [0] y-min (pts)
              800   [800] x-length (pts)
              800   [800] y-length (pts)
    field_fill   T   [T] F
    field_label   T   [T] F
    field_label_scale 0.75   [0.72] (rel)
    font   Helvetica
    grid   F   [F] T

```
half_ticks        T        [T] F
line_width        1.00     0-99 [1.] (pts)
picture_transformation :
            0.180    [0.18] x-scale (rel)
            0.180    [0.18] y-scale (rel)
            130.     [0.18] x-translation (pts)
            220.     [0.18] y-translation (pts)
            0.00     [0.0]  rotation (deg)
plot_aspect_ratio    1.000    [1.0] x_axis_length/y_axis_length
replicate_label      0.250    0->1 [0.025]
splines          T        [T] F
tenth_ticks      F        [F] T
text_scale       1.000    [1.] (rel)
```
To change these options edit or create the plot option file
See: www.perplex.ethz.ch/perplex_plot_options.html

PostScript will be written to file: ex2.ps

Modify the default plot (y/n)?
N

(3b) Modifying the default plotting of the calculated phase diagram (PSVDRAW)

E.g. you want to modify the axes numbering (intervals on x axis = 100°C; intervals on y axis = 4 kbar) and you want to assign a numeric label (rather than a text label) to (most of) the reaction curves.

Run again PSVDRAW:

C:\PERPLEX\Perplex686>psvdraw

Perple_X version 6.8.6, source updated Jan 24, 2019.
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Enter the project or plot file name [i.e., without the .plt suffix]:
Ex2

Perple_X plot options are currently set as:
```
  Keyword:        Value:    Permitted values [default]:
  axis_label_scale    1.20      [1.2] (rel)
  bounding_box :
                0     [0] x-min (pts)
                0     [0] y-min (pts)
              800     [800] x-length (pts)
              800     [800] y-length (pts)
  field_fill       T       [T] F
  field_label      T       [T] F
  field_label_scale   0.75      [0.72] (rel)
  font           Helvetica
  grid           F       [F] T
  half_ticks       T       [T] F
  line_width       1.00      0-99 [1.] (pts)
  picture_transformation :
              0.180     [0.18] x-scale (rel)
              0.180     [0.18] y-scale (rel)
              130.     [0.18] x-translation (pts)
              220.     [0.18] y-translation (pts)
              0.00     [0.0]  rotation (deg)
  plot_aspect_ratio    1.000     [1.0] x_axis_length/y_axis_length
  replicate_label     0.250     0->1 [0.025]
  splines         T       [T] F
  tenth_ticks       F       [F] T
  text_scale       1.000     [1.] (rel)
To change these options edit or create the plot option file
See: www.perplex.ethz.ch/perplex_plot_options.html
```

PostScript will be written to file: ex2.ps

Modify the default plot (y/n)?
y

Modify drafting options (y/n)?
  answer yes to modify:
   - x-y plotting limits
   - axes numbering
y

Modify x-y limits (y/n)?
Answer Y if you want to modify the T and/or P range of the diagram.
n

Restrict phase fields by variance (y/n)?
  answer yes to:
   - suppress pseudounivariant curves and/or pseudoinvariant points of a specified true variance.
This question is only relevant for more complex calculations, involving solution models and therefore considering also pseudo-univariant curves (i.e. di-variant equilibria involving two pseudocompounds of the same phase as reactant and product). *See Ex. 7*.
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
n

Modify default equilibrium labeling (y/n)?
  answer yes to:
   - modify/suppress [pseudo-] univariant curve labels
   - suppress [pseudo-] invariant point labels
y

Suppress curve labels (y/n)?
n

Change default labeling of curve segments (y/n)?
y

Suppress labels of pseudounivariant curves (y/n)?
y

Enter minimum fraction of the axes length that a curve must be to receive a text label (0-1):
1 means that a text label will be assigned to those curves that are longer than the axes length.
1

Enter minimum fraction of the axes length that a curve must be to receive a numeric label (0-1.000):
0 means that a numeric label will be assigned to all those curves that are shorter than the axes length.
0

Suppress point labels (y/n)?

n

Modify default axes numbering (y/n)?

y

Enter the starting value and interval for major tick marks on the X-axis (current values are: 473.   160.   )
Enter the new values:

473
100

Enter the starting value and interval for major tick marks on the Y-axis (current values are: 500. 0.390E+04)
Enter the new values:

1000
4000

Equilibria corresponding to each reaction number are explained in the ex2.prn file.

Ex. 3

Ex. 3 – Composition diagrams (chemographies) for the CMSH system

This exercise explains how to calculate composition diagrams (i.e. chemographies) for the P-T projection of Ex. 2, at the P-T conditions reported below as A-I.
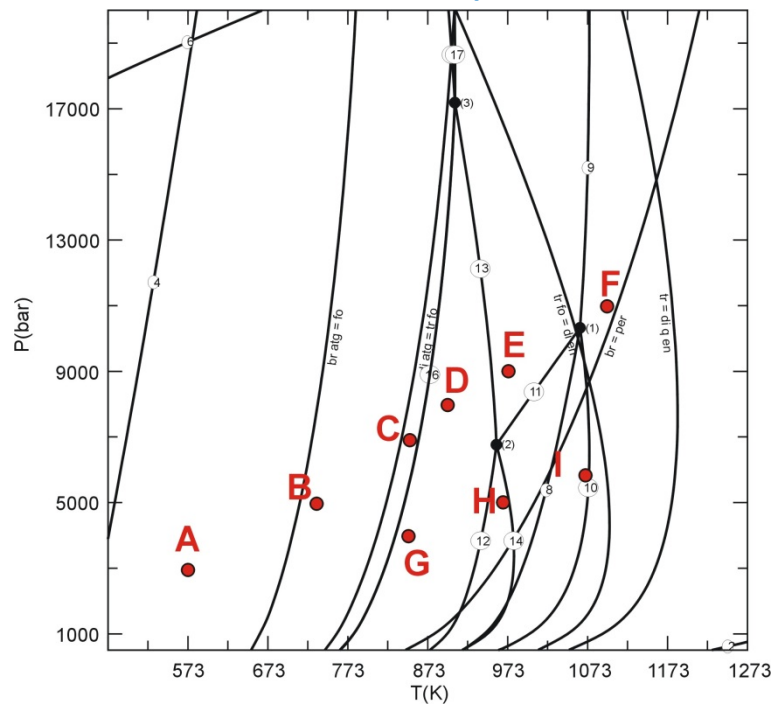
(1) Definition of the problem (BUILD)

C:\PERPLEX\Perplex686>build

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NO is the default (blank) answer to all Y/N prompts

Enter a name for this project (the name will be used as the root for all output file names) [default = my_project]:
Ex3

The problem definition file will be named: ex3.dat

Enter thermodynamic data file name [default = hp02ver.dat]:
hp62ver.dat

Enter the computational option file name [default = perplex_option.dat]:
See: www.perplex.ethz.ch/perplex_options.html
[enter]

Reading computational options from: perplex_option.dat

The current data base components are:

Na2O MgO Al2O3 SiO2 K2O CaO TiO2 MnO FeO NiO ZrO2 Cl2 O2   H2O CO2 CuO Cr2O3 S2   F2
Transform them (Y/N)?

n

Specify computational mode:
    1 - Convex-Hull minimization
    2 - Constrained minimization on a 2d grid [default]
    3 - Constrained minimization on a 1d grid
    4 - Output pseudocompound data
    5 - 1-d Phase fractionation calculations
    6 - 0-d Infiltration-reactionation-fractionation
    7 - 2-d Phase fractionation (FRAC2D and TITRATE reactive transport models)

Use Convex-Hull minimization for Schreinemakers projections or phase diagrams with > 2 independent variables. Use constrained minimization for phase diagrams or phase diagram sections with < 3 independent variables.

1

Use option 1 (Convex-Hull minimization) for PROJECTIONS (Schreinemakers-type diagrams) or CHEMOGRAPHIES (composition diagrams; phase diagrams with > 2 independent variables). Use options 2 or 3 (Constrained minimization on a 2d grid/1d grid) for PSEUDOSECTIONS (phase diagrams or phase diagram sections with < 3 independent variables).

Calculations with a saturated   FLUID (Y/N)?

y

Select the independent saturated   FLUID components:
 H2O   CO2
Enter names, 1 per line, press <enter> 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

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   CO2 CuO Cr2O3 S2   F2
Enter names, 1 per line, press <enter> to finish:

CaO

MgO

SiO2

The order (1st, 2nd, 3rd) influences how the three components are plotted in the chemographies: first = bottom left, second = bottom right, third = top.

Because the thermodynamic data file identifies: H2O as special components, you will be prompted next for the EoS to be used for the corresponding composants and mixtures thereof. To override this behavior, e.g., to use a generic hybrid fluid EoS, delete the special_component section from the thermodynamic data file header.

Select fluid equation of state:
  0 - X(CO2) H2O-CO2 Modified Redlich-Kwong (MRK) DeSantis et al 74
  1 - X(CO2) H2O-CO2 HSMRK Kerrick & Jacobs 81
  2 - X(CO2) H2O-CO2 MRK hybrid-EoS*
  5 - X(CO2) H2O-CO2 CORK Holland & Powell 91, 98
  8 - f(O2/CO2) C-buffered COH MRK hybrid-EoS*
  10 - X(O) C-buffered COH MRK hybrid-EoS Connolly & Cesare 93*
  12 - X(O)-f(S2) C-buffered COHS MRK hybrid-EoS Connolly & Cesare 93*
  13 - X(H2) H2O-H2 MRK hybrid-EoS*
  14 - X(CO2) H2O-CO2 Pitzer & Sterner 94; Holland & Powell mixing 03
  15 - X(H2) H2O-H2 low T MRK hybrid-EoS*
  16 - X(O) H-O MRK hybrid-EoS*
  17 - X(O)-f(S2) H-O-S MRK hybrid-EoS*
  19 - X(O)-X(S) C-buffered COHS MRK hybrid-EoS Connolly & Cesare 93*
  20 - X(O)-X(C) COHS MRK hybrid-EoS Connolly & Cesare 93*
  24 - f(O2/CO2)-N/C C-buffered COHN MRK hybrid-EoS*
  25 - X(CO2)-X(NaCl) H2O-CO2-NaCl Aranovich et al 10
  26 - X(O) O-Si MRK Connolly 16
  27 - X(O)-X(C) C-O-H MRK hybrid-EoS*
*Hybrid EoS use the following pure species EoS, to change these associations modify the hybrid_EoS keywords in the perplex_option file:
    H2O - PSEoS Pitzer & Sterner 1994
    CO2 - PSEoS Pitzer & Sterner 1994
    CH4 - HSMRK Kerrick & Jacobs 1981
5

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

Output a print file (Y/N)?
y

warning ver051 cannot make hmjL because of missing data or an invalid definition in the thermodynamic data file.
…

Exclude pure and/or endmember phases (Y/N)?
y
Do you want to be prompted for phases (Y/N)?

N

Enter names, 1 per line, press <enter> to finish:
Same as in Ex2.
cumm_dqf
fo8L
q8L
cenjh
odi
qjL
dijL
fojL
foTL
mcpv
cmpv
foHL
qHL
ak
chum
lrn
merw
mont
rnk
cen
cpv
cstn
cumm
wo
pswo
wal
woL
limL

Include solution models (Y/N)?
N

Enter calculation title:
Ex3

*Although only one component is specified for the   FLUID   phase, its equation of state permits use of its compositional variable: Y(CO2) .

Specify values for: P(bar)   T(K)   Y(CO2). For calculation 1, enter zeros to finish.
Here you must specify at which P-T-XCO2 conditions you would like to calculate the chemographies. Having included only H_2O as saturated fluid component, XCO_2 is always 0.
Point A:
3000
573

0

Specify values for: P(bar) T(K)   Y(CO2). For calculation 2, enter zeros to finish.

Point B:

5000

733

0

Specify values for: P(bar) T(K)   Y(CO2). For calculation 3, enter zeros to finish.

Point C:

7000

843

0

Specify values for: P(bar) T(K)   Y(CO2). For calculation 4, enter zeros to finish.

Point D:

8000

893

0

Specify values for: P(bar) T(K)   Y(CO2). For calculation 5, enter zeros to finish.

Point E:

9000

973

0

Specify values for: P(bar) T(K)   Y(CO2). For calculation 6, enter zeros to finish.

Point F:

11000

1093

0

Specify values for: P(bar) T(K)   Y(CO2). For calculation 7, enter zeros to finish.

Point G:

4000

843

0

Specify values for: P(bar) T(K)   Y(CO2). For calculation 8, enter zeros to finish.

Point H:

5000

963

0

Specify values for: P(bar) T(K)   Y(CO2). For calculation 9, enter zeros to finish.

Point I:

6000

1073

0

Specify values for:.   P(bar)   T(K)   Y(CO2) For calculation 10, enter zeros to finish.
0
0
0

(2) Doing the calculation (CONVEX)

Run CONVEX to make the calculation:

C:\PERPLEX\Perplex686>convex

Perple_X version 6.8.6, source updated Jan 24, 2019.
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Enter the project name (the name assigned in BUILD) [default = my_project]:
Ex3

Reading problem definition from file: ex3.dat
Reading thermodynamic data from file: hp62ver.dat
Reading solution models from file: not requested
Writing print output to file: ex3.prn
Writing plot output to file: ex3.plt
Reading Perple_X options from: perplex_option.dat
Writing Perple_X option summary to file: not requested

Perple_X version 6.8.6, source updated Jan 24, 2019.
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Perple_X computational option settings for CONVEX:
   Keyword: Value: Permitted values [default]:
  Auto-refine options:
   auto_refine   man   off manual [auto]
  Solution subdivision options:
   initial_resolution:
     exploratory stage   0.0625   0->1 [1/16], 0 => off
     auto-refine stage   0.0063   0->1 [1/160], 0 => off
   stretch_factor   0.0020   >0 [2d-3]
   subdivision_override off   [off] lin str
   hard_limits   off   [off] on
   refine_endmembers   F   [F] T
   pc_perturbation   0.0050   [5d-3]
  Thermodynamic options:
   solvus_tolerance   aut   [aut] or 0->1; aut = automatic, 0 => p=c pseudocompounds, 1 => homogenize
   T_stop (K)   0.0   [0]
   T_melt (K)   873.0   [873]
   order_check   on   off [on]
   approx_alpha   T   [T] F
   Anderson-Gruneisen   F   [F] T

```
  speciation_factor      100.    >10 [100] speciation precision = final resolution/speciation_factor
  speciation_max_it     100     [100]
  hybrid_EoS_H2O         4     [4] 0-2, 4-7
  hybrid_EoS_CO2         4     [4] 0-4, 7
  hybrid_EoS_CH4         0     [0] 0-1, 7
  aq_bad_results        err     [err] 101, 102, 103, ignore
  aq_lagged_speciation  F       [F] T
  aq_ion_H+          T       [T] F => use OH-
  aq_oxide_components   F       [F] T
  aq_solvent_solvus    T       [T] F
  aq_vapor_epsilon     1.0     [1.]
 Input/Output options:
  dependent_potentials   off      off [on]
  pause_on_error       T       [T] F
  auto_exclude        T       [T] F
 Worst case (Cartesian) compositional resolution (mol):
  Exploratory stage:   0.521E-2
  Auto-refine stage:   0.521E-3
 Adapative minimization will be done with:
  4 iterations in the exploratory stage
  4 iterations in the autorefine stage
To change these options see: www.perplex.ethz.ch/perplex_options.html
```

warning ver051 cannot make hmjL   because of missing data or an invalid definition in the thermodynamic data file.

…

```
** Starting auto_refine computational stage **
Computing the compositional phase relations at condition  1
 cycle      1      1      1
 cycle      2      2      3
 cycle      3      4      5
 cycle      4      6      7
Computing the compositional phase relations at condition  2
 cycle      1      1      1
 cycle      2      2      3
 cycle      3      4      5
 cycle      4      6      7
 cycle      5      8      8
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
Computing the compositional phase relations at condition  4
 cycle      1      1      1
 cycle      2      2      3
 cycle      3      4      5
 cycle      4      6      7
Computing the compositional phase relations at condition  5
```

```
cycle       1       1       1
cycle       2       2       3
cycle       3       4       5
cycle       4       6       7
cycle       5       8       8
Computing the compositional phase relations at condition  6
cycle       1       1       1
cycle       2       2       3
cycle       3       4       5
cycle       4       6       7
Computing the compositional phase relations at condition  7
cycle       1       1       1
cycle       2       2       3
cycle       3       4       5
cycle       4       6       7
Computing the compositional phase relations at condition  8
cycle       1       1       1
cycle       2       2       3
cycle       3       4       5
cycle       4       6       7
cycle       5       8       8
Computing the compositional phase relations at condition  9
cycle       1       1       1
cycle       2       2       3
cycle       3       4       5
cycle       4       6       7
cycle       5       8       8
```

(3) Plotting the calculated phase diagram (PSVDRAW)

Run PSVDRAW to plot the calculated chemographies:

C:\PERPLEX\Perplex686>PSVDRAW

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Enter the project or plot file name [i.e., without the .plt suffix]:
EX3

Perple_X plot options are currently set as:

Keyword:	Value:	Permitted values [default]:
axis_label_scale	1.20	[1.2] (rel)
bounding_box :		
	0	[0] x-min (pts)
	0	[0] y-min (pts)
	800	[800] x-length (pts)
	800	[800] y-length (pts)
field_fill	T	[T] F
field_label	T	[T] F

```
field_label_scale    0.75      [0.72] (rel)
font            Helvetica
grid            F       [F] T
half_ticks      T       [T] F
line_width         1.00     0-99 [1.] (pts)
picture_transformation :
               0.180    [0.18] x-scale (rel)
               0.180    [0.18] y-scale (rel)
                130.    [0.18] x-translation (pts)
                220.    [0.18] y-translation (pts)
               0.00    [0.0]  rotation (deg)
plot_aspect_ratio    1.000     [1.0] x_axis_length/y_axis_length
replicate_label    0.250     0->1 [0.025]
splines         T       [T] F
tenth_ticks     F       [F] T
text_scale        1.000     [1.] (rel)
```

To change these options edit or create the plot option file
See: www.perplex.ethz.ch/perplex_plot_options.html

PostScript will be written to file: EX3.ps

Modify the default plot (y/n)?
N

P(bar) =0.300E+04
T(K) = 573.
Y(CO2) = 0.00

P(bar) =0.500E+04
T(K) = 733.
Y(CO2) = 0.00

P(bar) =0.700E+04
T(K) = 843.
Y(CO2) = 0.00

P(bar) =0.800E+04
T(K) = 893.
Y(CO2) = 0.00

P(bar) =0.900E+04
T(K) = 973.
Y(CO2) = 0.00

P(bar) =0.110E+05
T(K) =0.109E+04
Y(CO2) = 0.00

P(bar) =0.400E+04
T(K) = 843.
Y(CO2) = 0.00

P(bar) =0.500E+04
T(K) = 963.
Y(CO2) = 0.00

P(bar) =0.600E+04
T(K) =0.107E+04
Y(CO2) = 0.00
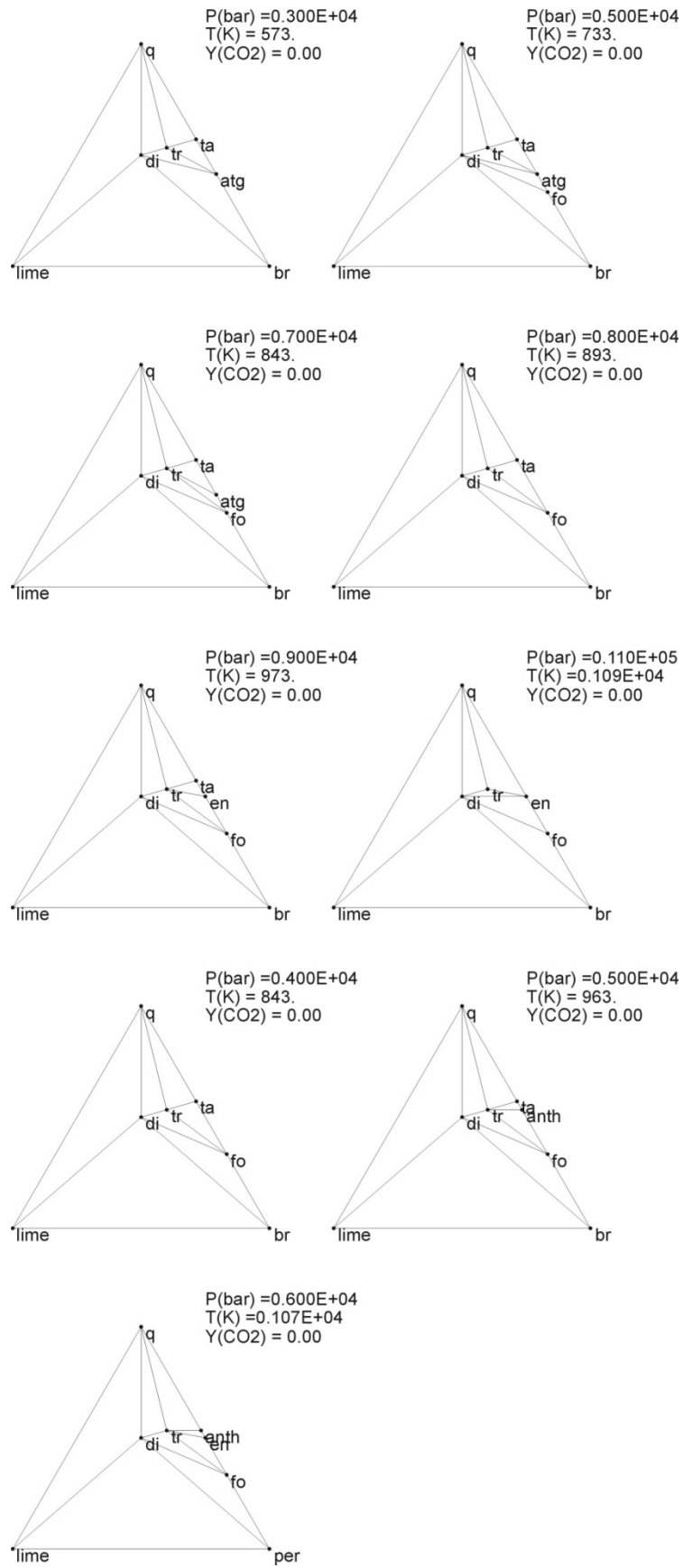
Ex. 4

Ex. 4 – P-T pseudosection for the CMSH system (no solid solutions)

This exercise explains how to calculate a very simple pseudosection, <u>not involving solid solutions</u>, for a generic ultramafic composition (MgO=50, SiO₂=45, CaO=5 mol%; red dot in the figure below).
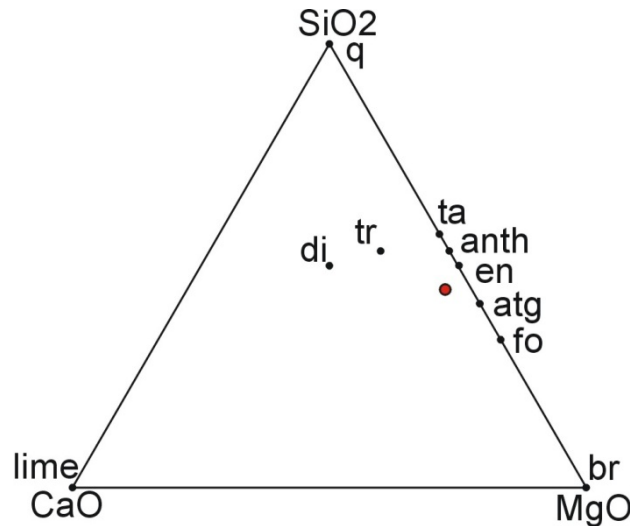
Combined with Ex. 2 and Ex. 3, this exercise is useful to understand the difference between P-T projections and P-T pseudosections.

(1) Definition of the problem (BUILD)

C:\PERPLEX\Perplex686>build

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NO is the default (blank) answer to all Y/N prompts

Enter a name for this project (the name will be used as the root for all output file names) [default = my_project]:
Ex4

The problem definition file will be named: ex4.dat

Enter thermodynamic data file name [default = hp02ver.dat]:
hp62ver.dat

Enter the computational option file name [default = perplex_option.dat]:
See: www.perplex.ethz.ch/perplex_options.html
[enter]

Reading computational options from: perplex_option.dat

The current data base components are:

Na2O MgO Al2O3 SiO2 K2O CaO TiO2 MnO FeO NiO ZrO2 Cl2 O2   H2O CO2 CuO Cr2O3 S2
F2

Transform them (Y/N)?

n

Specify computational mode:

    1 - Convex-Hull minimization
    2 - Constrained minimization on a 2d grid [default]
    3 - Constrained minimization on a 1d grid
    4 - Output pseudocompound data
    5 - 1-d Phase fractionation calculations
    6 - 0-d Infiltration-reactionation-fractionation
    7 - 2-d Phase fractionation (FRAC2D and TITRATE reactive transport models)

Use Convex-Hull minimization for Schreinemakers projections or phase diagrams with > 2 independent variables. Use constrained minimization for phase diagrams or phase diagram sections with < 3 independent variables.

2

Use option 1 (Convex-Hull minimization) for PROJECTIONS (Schreinemakers-type diagrams) or CHEMOGRAPHIES (composition diagrams; phase diagrams with > 2 independent variables). Use options 2 or 3 (Constrained minimization on a 2d grid/1d grid) for PSEUDOSECTIONS (phase diagrams or phase diagram sections with < 3 independent variables).

Calculations with a saturated FLUID (Y/N)?

y

Select the independent saturated   FLUID components:
 H2O   CO2
Enter names, 1 per line, press <enter> 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

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   CO2 CuO Cr2O3 S2   F2
Enter names, 1 per line, press <enter> to finish:

MgO

SiO2

CaO

Because the thermodynamic data file identifies: H2O as special components, you will be prompted next for the EoS to be used for the corresponding composants and mixtures thereof. To override this behavior, e.g., to use a generic hybrid fluid EoS, delete the special_component section from the thermodynamic data file header.

Select fluid equation of state:
  0 - X(CO2) H2O-CO2 Modified Redlich-Kwong (MRK) DeSantis et al 74
  1 - X(CO2) H2O-CO2 HSMRK Kerrick & Jacobs 81
  2 - X(CO2) H2O-CO2 MRK hybrid-EoS*
  5 - X(CO2) H2O-CO2 CORK Holland & Powell 91, 98
  8 - f(O2/CO2) C-buffered COH MRK hybrid-EoS*
  10 - X(O) C-buffered COH MRK hybrid-EoS Connolly & Cesare 93*
  12 - X(O)-f(S2) C-buffered COHS MRK hybrid-EoS Connolly & Cesare 93*
  13 - X(H2) H2O-H2 MRK hybrid-EoS*
  14 - X(CO2) H2O-CO2 Pitzer & Sterner 94; Holland & Powell mixing 03
  15 - X(H2) H2O-H2 low T MRK hybrid-EoS*
  16 - X(O) H-O MRK hybrid-EoS*
  17 - X(O)-f(S2) H-O-S MRK hybrid-EoS*
  19 - X(O)-X(S) C-buffered COHS MRK hybrid-EoS Connolly & Cesare 93*
  20 - X(O)-X(C) COHS MRK hybrid-EoS Connolly & Cesare 93*
  24 - f(O2/CO2)-N/C C-buffered COHN MRK hybrid-EoS*
  25 - X(CO2)-X(NaCl) H2O-CO2-NaCl Aranovich et al 10
  26 - X(O) O-Si MRK Connolly 16
  27 - X(O)-X(C) C-O-H MRK hybrid-EoS*
*Hybrid EoS use the following pure species EoS, to change these associations modify the hybrid_EoS keywords in the perplex_option file:
    H2O - PSEoS Pitzer & Sterner 1994
    CO2 - PSEoS Pitzer & Sterner 1994
    CH4 - HSMRK Kerrick & Jacobs 1981
5

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

Select x-axis variable:
    1 - P(bar)
    2 - T(K)
    3 - Y(CO2)
    4 - Composition X(C1)* (user defined)
*Although only one component is specified for the Y(CO2) phase, its equation of state permits use of its compositional variable: *X(C1) can not be selected as the y-axis variable
2

Enter minimum and maximum values, respectively, for: T(K)
473
1273

Select y-axis variable:
    2 - P(bar)
    3 - Y(CO2)

2

Enter minimum and maximum values, respectively, for: P(bar)
500
20000

Specify sectioning value for: Y(CO2)
0

For gridded minimization, grid resolution is determined by the number of levels (grid_levels) and the resolution at the lowest level in the X- and Y-directions (x_nodes and y_nodes) these parameters are currently set for the exploratory and autorefine cycles as follows:

stage   grid_levels xnodes ynodes   effective resolution
exploratory   1   40   40   40 x 40 nodes
auto-refine   4   60   60   473 x 473 nodes

To change these options edit or create the file perplex_option.dat
See: www.perplex.ethz.ch/perplex_options.html#grid_parameters

Specify component amounts by mass (Y/N)?
N

Here you can specify the bulk composition of your sample either in wt% (by mass) or in mol%. In this example, that refers to a generic ultramafic rock rather than to a real sample, I have chosen mol% because it is easier to visualize a mol% composition on the chemographies.

Enter molar amounts of the components:
 MgO   SiO2 CaO
for the bulk composition of interest:
50
45
5

Output a print file (Y/N)?
Y

warning ver051 cannot make hmjL   because of missing data or an invalid definition in the thermodynamic data file.
…

Exclude pure and/or endmember phases (Y/N)?
Y
Do you want to be prompted for phases (Y/N)?
N

Enter names, 1 per line, press <enter> to finish:
Same as in Ex2 and Ex3.
cumm_dqf
fo8L
q8L

cenjh

odi

qjL

dijL

fojL

foTL

mcpv

cmpv

foHL

qHL

ak

chum

lrn

merw

mont

rnk

cen

cpv

cstn

cumm

wo

pswo

wal

woL

limL

Include solution phases (Y/N)?
N

Enter calculation title:
Ex4

(2) Doing the calculation (VERTEX)

Run VERTEX to make the calculation:

C:\PERPLEX\Perplex686>vertex

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Enter the project name (the name assigned in BUILD) [default = my_project]:
Ex4

Reading problem definition from file: ex4.dat
Reading thermodynamic data from file: hp62ver.dat
Reading solution models from file: not requested

Writing print output to file: ex4.prn
Writing plot output to file: ex4.plt
Writing bulk composition plot output to file: ex4.blk
Reading Perple_X options from: perplex_option.dat
Writing Perple_X option summary to file: not requested

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Perple_X computational option settings for VERTEX:
   Keyword: Value: Permitted values [default]:
  Auto-refine options:
   auto_refine   man   off manual [auto]
  Free energy minimization options:
   final_resolution:
     exploratory stage   0.1E-1   [1e-2], target value, see actual values be low
     auto-refine stage   0.1E-2   [1e-3], target value, see actual values be low
   resolution_factor   2   >= 2 [2]
   refinement_points   5   [aut] or 1->12; aut = automatic
   solvus_tolerance_II aut   0->1 [0.2]
   global_reach_increment 0   >= 0 [0]
   reach_increment_switch on   [on] off all
   zero_mode   0.1E-05 0->1 [1e-6]; < 0 => off
  2D grid options:
   x_nodes   40 / 40   [20/40], >0, <2048; effective x-resolution
60 / 473 nodes
   y_nodes   40 / 40   [20/40], >0, <2048; effective y-resolution
60 / 473 nodes
   grid_levels   1 / 4   [1/4], >0, <10
   linear_model   on   off [on]
  Solution subdivision options:
   initial_resolution:
     exploratory stage   0.0625   0->1 [1/16], 0 => off
     auto-refine stage   0.0208   0->1 [1/48], 0 => off
   stretch_factor   0.0020   >0 [2d-3]
   subdivision_override off   [off] lin str
   hard_limits   off   [off] on
   refine_endmembers   F   [F] T
  Thermodynamic options:
   solvus_tolerance   aut   [aut] or 0->1; aut = automatic, 0 => p=c pseudocompounds, 1 => homogenize
   T_stop (K)   0.0   [0]
   T_melt (K)   873.0   [873]
   order_check   on   off [on]
   approx_alpha   T   [T] F
   Anderson-Gruneisen   F   [F] T
   speciation_factor   100.   >10 [100] speciation precision = final resolution/speciation_factor
   speciation_max_it   100   [100]
   hybrid_EoS_H2O   4   [4] 0-2, 4-7
   hybrid_EoS_CO2   4   [4] 0-4, 7
   hybrid_EoS_CH4   0   [0] 0-1, 7
   aq_bad_results   err   [err] 101, 102, 103, ignore

```
  aq_lagged_speciation   F        [F] T
  aq_ion_H+            T        [T] F => use OH-
  aq_oxide_components    F        [F] T
  aq_solvent_solvus     T        [T] F
  aq_vapor_epsilon      1.0      [1.]
 Input/Output options:
  dependent_potentials   off      off [on]
  pause_on_error        T        [T] F
  auto_exclude          T        [T] F
  logarithmic_p         F        [F] T
  bad_number            NaN      [NaN]
  interim_results       aut      [auto] off manual
 Information file output options:
  option_list_files     F        [F] T; echo computational options
  pseudocompound_file    F        [F] T; echo static pseudocompound compositions
  auto_refine_file      F        [F] T; echo auto-refine compositions
 Worst case (Cartesian) compositional resolution (mol):
  Exploratory stage:   0.521E-2
  Auto-refine stage:   0.868E-3
 Adapative minimization will be done with:
   4 iterations in the exploratory stage
   5 iterations in the autorefine stage
To change these options see: www.perplex.ethz.ch/perplex_options.html
```

warning ver051 cannot make hmjLbecause of missing data or an invalid definition in the thermodynamic data file.
…

** Starting auto_refine computational stage **
 0.3% done with low level grid.
 2.9% done with low level grid.
 5.4% done with low level grid.
 8.0% done with low level grid.
10.5% done with low level grid.
13.1% done with low level grid.
15.7% done with low level grid.
18.2% done with low level grid.
20.8% done with low level grid.
23.3% done with low level grid.
25.9% done with low level grid.
28.4% done with low level grid.
31.0% done with low level grid.
33.5% done with low level grid.
36.1% done with low level grid.
38.7% done with low level grid.
41.2% done with low level grid.
43.8% done with low level grid.
46.3% done with low level grid.
48.9% done with low level grid.
51.4% done with low level grid.
54.0% done with low level grid.
56.5% done with low level grid.

59.1% done with low level grid.
61.7% done with low level grid.
64.2% done with low level grid.
66.8% done with low level grid.
69.3% done with low level grid.
71.9% done with low level grid.
74.4% done with low level grid.
77.0% done with low level grid.
79.6% done with low level grid.
82.1% done with low level grid.
84.7% done with low level grid.
87.2% done with low level grid.
89.8% done with low level grid.
92.3% done with low level grid.
94.9% done with low level grid.
97.4% done with low level grid.
100.0% done with low level grid.

Beginning grid refinement stage.
   197 grid cells to be refined at grid level 2
      refinement at level 2 involved   429 minimizations
  2029 minimizations required of the theoretical limit of   6241
   380 grid cells to be refined at grid level 3
      ...working (73 minimizations done)
      ...working (576 minimizations done)
      refinement at level 3 involved   745 minimizations
  2774 minimizations required of the theoretical limit of   24649
   719 grid cells to be refined at grid level 4
      ...working (333 minimizations done)
      ...working (834 minimizations done)
      ...working (1336 minimizations done)
      refinement at level 4 involved   1363 minimizations
  4137 minimizations required of the theoretical limit of   98596

(3) Plotting the calculated phase diagram (PSSECT)

Run PSSECT to plot the calculated pseudosection:

C:\PERPLEX\Perplex686>pssect

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Enter the project name (the name assigned in BUILD) [default = my_project]:
Ex4

Reading Perple_X options from: perplex_option.dat
Perple_X plot options are currently set as:
      Keyword: Value: Permitted values [default]:
   axis_label_scale   1.20   [1.2] (rel)

bounding_box :

0	[0]	x-min (pts)
0	[0]	y-min (pts)
800	[800]	x-length (pts)
800	[800]	y-length (pts)

field_fill   T   [T] F
field_label   T   [T] F
field_label_scale   0.75   [0.72] (rel)
font   Helvetica
grid   F   [F] T
half_ticks   T   [T] F
line_width   1.00   0-99 [1.] (pts)
picture_transformation :

0.180	[0.18]	x-scale (rel)
0.180	[0.18]	y-scale (rel)
130.	[0.18]	x-translation (pts)
220.	[0.18]	y-translation (pts)
0.00	[0.0]	rotation (deg)

plot_aspect_ratio   1.000   [1.0] x_axis_length/y_axis_length
replicate_label   0.250   0->1 [0.025]
splines   T   [T] F
tenth_ticks   F   [F] T
text_scale   1.000   [1.] (rel)
To change these options edit or create the plot option file
See: www.perplex.ethz.ch/perplex_plot_options.html

PostScript will be written to file: ex4.ps

Modify the default plot (y/n)?
n

ex4

Y(CO2) = 0.00
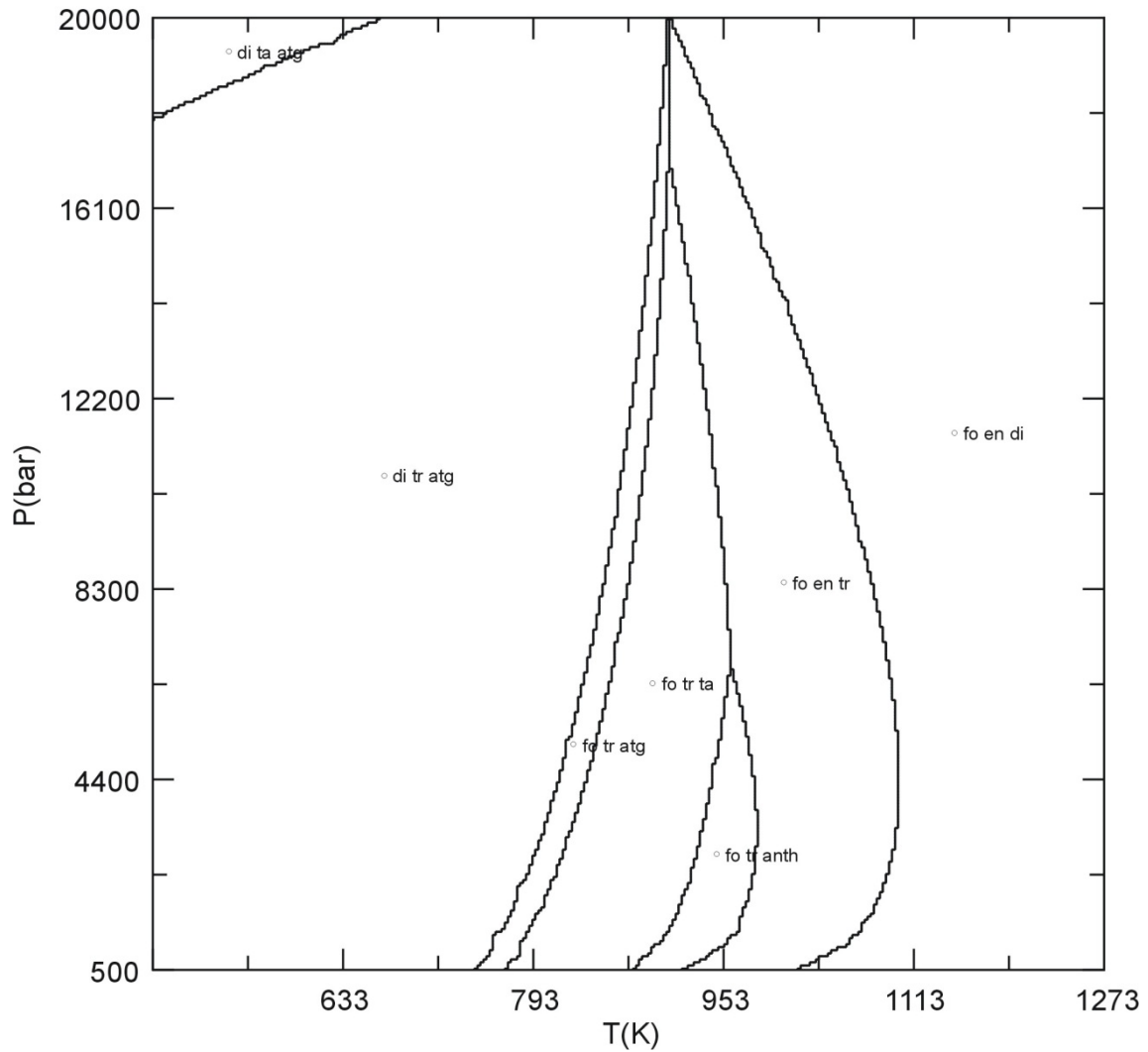
Being a very simple pseudosection (no solid solutions!), the stability fields of each mineral assemblage are separated by "real" reaction curves, i.e. UNIVARIANT CURVES, and all the field assemblages have the same variance. However, this is a very special case: pseudosections generally contain multi-variant field assemblages.

NB. The variance of each field is 2 [f= c-p+2; c=4 (CMSH); p=4 (remember that each field also contains H_2O)]

(4) Comparison between projection and pseudosection
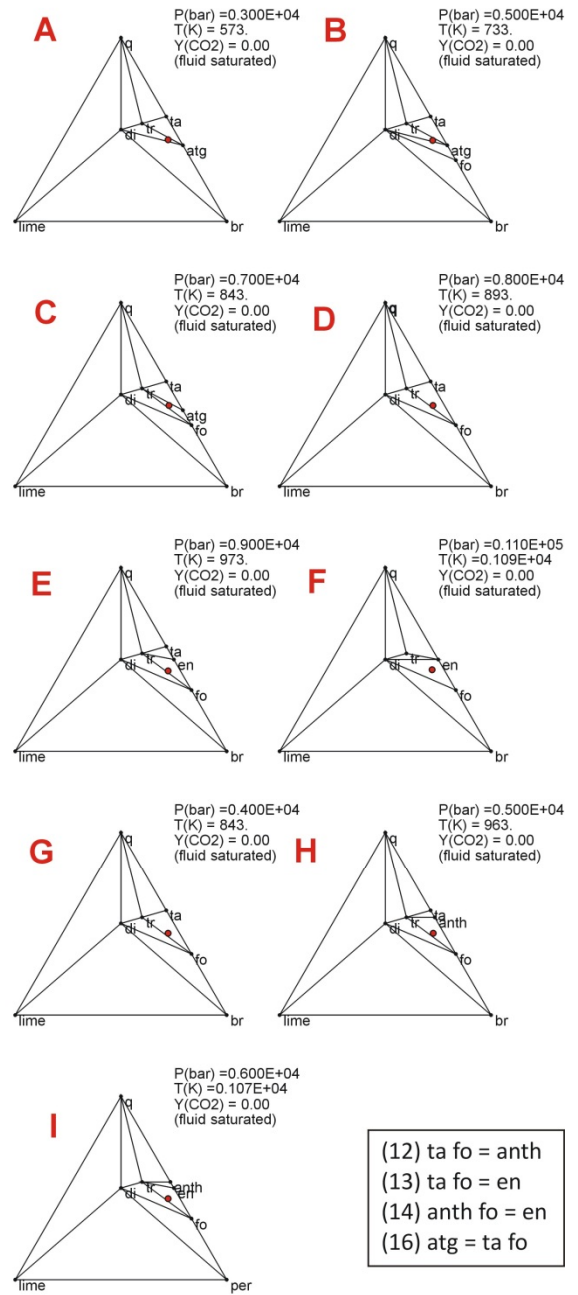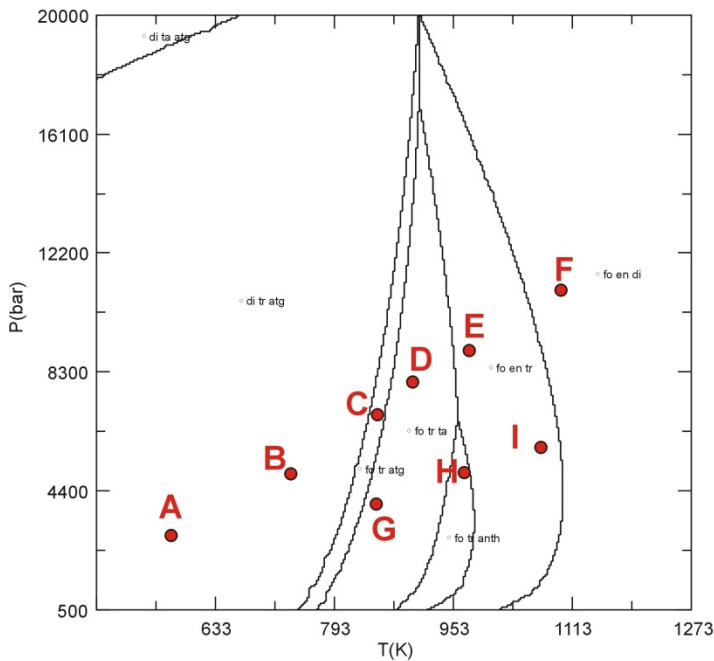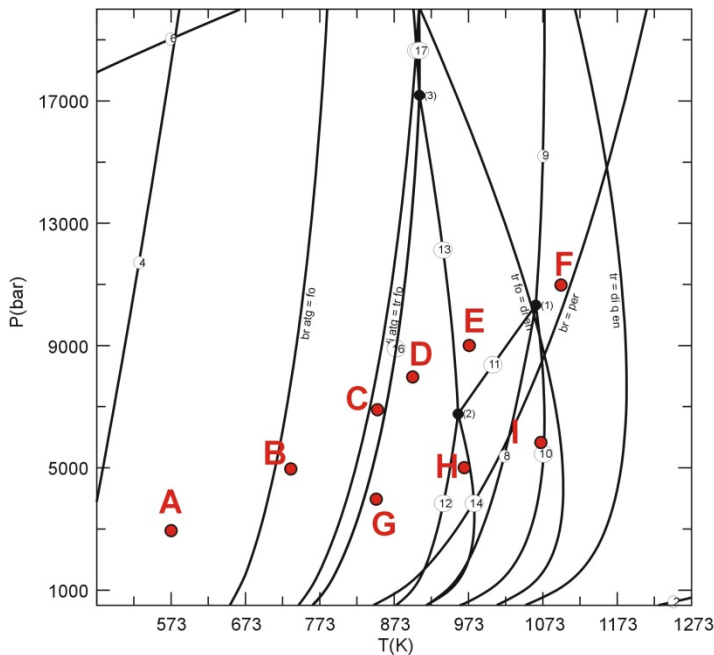
Comparison between the CMSH projection (Ex. 2) and the pseudosection (Ex. 4) calculated for a bulk composition MgO=50 mol%, SiO2=45 mol%, CaO=5 mol% (red dot in the chemographies – Ex. 3).

This specific bulk composition "sees" (i.e. is sensible to) only some of the reactions predicted by the P-T projection.

Ex. 5

Ex. 5 – T-X(CO₂) projections and pseudosections for the CMS-H₂O-CO₂ system (no solid solutions)

This exercise investigates prograde metamorphism of impure dolomites and limestones characterized by different amounts of Cal, Dol and Qtz. A constant pressure of 1 kbar, typical of shallow level contact aureoles, is considered.

This exercise is useful to understand the difference between T-X(CO₂) projections and T-X(CO₂) pseudosections and allows you to become familiar with the use of H₂O-CO₂ fluids.

Ex. 5.1 – Isobaric T-X(CO₂) projection for a generic siliceous dolomite containing excess Cal

(1) Definition of the problem (BUILD)

C:\PERPLEX\Perplex686>build

Perple_X version 6.8.6, source updated Jan 24, 2019.
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NO is the default (blank) answer to all Y/N prompts

Enter a name for this project (the name will be used as the root for all output file names) [default = my_project]:
Ex5_1

The problem definition file will be named: ex5_1.dat

Enter thermodynamic data file name [default = hp02ver.dat]:
hp62ver.dat

Enter the computational option file name [default = perplex_option.dat]:
See: www.perplex.ethz.ch/perplex_options.html
enter

Reading computational options from: perplex_option.dat

The current data base components are:
Na2O MgO Al2O3 SiO2 K2O CaO TiO2 MnO FeO NiO ZrO2 Cl2 O2 H2O CO2 CuO Cr2O3 S2 F2
Transform them (Y/N)?
n

Specify computational mode:
    1 - Convex-Hull minimization
    2 - Constrained minimization on a 2d grid [default]
    3 - Constrained minimization on a 1d grid
    4 - Output pseudocompound data

5 - 1-d Phase fractionation calculations

6 - 0-d Infiltration-reactionation-fractionation

7 - 2-d Phase fractionation (FRAC2D and TITRATE reactive transport models)

Use Convex-Hull minimization for Schreinemakers projections or phase diagrams with > 2 independent variables. Use constrained minimization for phase diagrams or phase diagram sections with < 3 independent variables.

1

Calculations with a saturated FLUID (Y/N)?

y

Select the independent saturated FLUID components:

 H2O   CO2

Enter names, 1 per line, press <enter> 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

Because we want to calculate a T-XCO2 grid, both H2O and CO2 must be included in the calculation.

Calculations with saturated components (Y/N)?

Y

We want to calculate the T-XCO2 grid with **calcite in excess**, therefore we must consider CaO as a saturated component.

warning ver015 if you select > 1 saturated component, then the order you enter the components determines the saturation hierarchy and may effect your results (see Connolly 1990).

NOTE: If more than one saturated component is specified Perple_X applies the constraints sequentially.

For example, if CaO and MgO are specified as saturated components in this order, this implies that calcite and dolomite would be excess phases; if the order is reversed (MgO, CaO) then, at the same conditions, the stable phases would be magnesite and calcite. This sequence is referred to as the saturation hierarchy.

Select < 6 saturated components from the set:

 Na2O MgO Al2O3 SiO2 K2O CaO TiO2 MnO FeO NiO ZrO2 Cl2 O2   CuO Cr2O3 S2   F2

Enter names, 1 per line, press <enter> to finish:

CaO

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

N

Select thermodynamic components from the set:

 Na2O Al2O3 SiO2 K2O   TiO2 MnO FeO NiO ZrO2 Cl2 O2   CuO Cr2O3 S2   F2

Enter names, 1 per line, press <enter> to finish:

MgO

SiO2

Because the thermodynamic data file identifies: H2O   CO2 as special components, you will be prompted next for the EoS to be used for the corresponding composants and mixtures thereof. To override this behavior, e.g., to use a generic hybrid fluid EoS, delete the special_component section from the thermodynamic data file header.

Select fluid equation of state:
   0 - X(CO2) H2O-CO2 Modified Redlich-Kwong (MRK) DeSantis et al 74
   1 - X(CO2) H2O-CO2 HSMRK Kerrick & Jacobs 81
   2 - X(CO2) H2O-CO2 MRK hybrid-EoS*
   5 - X(CO2) H2O-CO2 CORK Holland & Powell 91, 98
   8 - f(O2/CO2) C-buffered COH MRK hybrid-EoS*
   10 - X(O) C-buffered COH MRK hybrid-EoS Connolly & Cesare 93*
   12 - X(O)-f(S2) C-buffered COHS MRK hybrid-EoS Connolly & Cesare 93*
   13 - X(H2) H2O-H2 MRK hybrid-EoS*
   14 - X(CO2) H2O-CO2 Pitzer & Sterner 94; Holland & Powell mixing 03
   15 - X(H2) H2O-H2 low T MRK hybrid-EoS*
   16 - X(O) H-O MRK hybrid-EoS*
   17 - X(O)-f(S2) H-O-S MRK hybrid-EoS*
   19 - X(O)-X(S) C-buffered COHS MRK hybrid-EoS Connolly & Cesare 93*
   20 - X(O)-X(C) COHS MRK hybrid-EoS Connolly & Cesare 93*
   24 - f(O2/CO2)-N/C C-buffered COHN MRK hybrid-EoS*
   25 - X(CO2)-X(NaCl) H2O-CO2-NaCl Aranovich et al 10
   26 - X(O) O-Si MRK Connolly 16
   27 - X(O)-X(C) C-O-H MRK hybrid-EoS*
*Hybrid EoS use the following pure species EoS, to change these associations modify the hybrid_EoS keywords in the perplex_option file:
    H2O - PSEoS Pitzer & Sterner 1994
    CO2 - PSEoS Pitzer & Sterner 1994
    CH4 - HSMRK Kerrick & Jacobs 1981
5

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
2

Select x-axis variable:
    1 - P(bar)
    2 - T(K)
    3 - Y(CO2)
3

Enter minimum and maximum values, respectively, for: Y(CO2)
0
1

Select y-axis variable:
    2 - T(K)
    3 - P(bar)

2

Enter minimum and maximum values, respectively, for: T(K)
573
873

Specify sectioning value for: P(bar)
1000

Output a print file (Y/N)?
Y
warning ver051 cannot make hmjL because of missing data or an invalid definition in the thermodynamic data file
…

Exclude pure and/or endmember phases (Y/N)?
Y
Do you want to be prompted for phases (Y/N)?
n
Enter names, 1 per line, press <enter> to finish:
cumm_dqf
fo8L
q8L
cenjh
odi
qjL
dijL
fojL
foTL
mcpv
cmpv
foHL
qHL
lrn
spu
merw
ty
mont
rnk
ak
cen

Include solution phases (Y/N)?
N

Enter calculation title:
Ex5_1

(2) Doing the calculation (CONVEX)

Run CONVEX to make the calculation:

C:\PERPLEX\Perplex686>convex

Perple_X version 6.8.6, source updated Jan 24, 2019.
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Enter the project name (the name assigned in BUILD) [default = my_project]:
Ex5_1

Reading problem definition from file: ex5_1.dat
Reading thermodynamic data from file: hp62ver.dat
Reading solution models from file: not requested
Writing print output to file: ex5_1.prn
Writing plot output to file: ex5_1.plt
Reading Perple_X options from: perplex_option.dat
Writing complete reaction list to file: not requested
Writing Perple_X option summary to file: not requested

Perple_X version 6.8.6, source updated Jan 24, 2019.
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Perple_X computational option settings for CONVEX:
    Keyword: Value: Permitted values [default]:
  Auto-refine options:
    auto_refine   man   off manual [auto]
  Schreinemakers and Mixed-variable diagram options:
    variance   1 /99   [1/99], >0, maximum true variance
    increment   0.100/0.025   [0.1/0.025], default search/trace variable
increment
    efficiency   3   [3] >0 < 6
    reaction_format   min   [min] full stoichiometry S+V everything
    reaction_list   off   [off] on
    console_messages   on   [on] off
    short_print_file   on   [on] off
  Solution subdivision options:
    initial_resolution:
      exploratory stage   0.0625   0->1 [1/16], 0 => off
      auto-refine stage   0.0208   0->1 [1/48], 0 => off
    stretch_factor   0.0020   >0 [2d-3]
    subdivision_override off   [off] lin str
    hard_limits   off   [off] on
    refine_endmembers   F   [F] T
    pc_perturbation   0.0050   [5d-3]
  Thermodynamic options:
    solvus_tolerance   aut   [aut] or 0->1; aut = automatic, 0 => p=c pseudocompounds, 1 => homogenize
    T_stop (K)   0.0   [0]
    T_melt (K)   873.0   [873]

order_check   on   off [on]
approx_alpha   T   [T] F
Anderson-Gruneisen   F   [F] T
speciation_factor   100.   >10 [100] speciation precision = final resolution/speciation_factor
speciation_max_it   100   [100]
hybrid_EoS_H2O   4   [4] 0-2, 4-7
hybrid_EoS_CO2   4   [4] 0-4, 7
hybrid_EoS_CH4   0   [0] 0-1, 7
aq_bad_results   err   [err] 101, 102, 103, ignore
aq_lagged_speciation F   [F] T
aq_ion_H+   T   [T] F => use OH-
aq_oxide_components   F   [F] T
aq_solvent_solvus   T   [T] F
aq_vapor_epsilon   1.0   [1.]
 Input/Output options:
  dependent_potentials   off   off [on]
  pause_on_error   T   [T] F
  auto_exclude   T   [T] F
 Worst case (Cartesian) compositional resolution (mol):
  Exploratory stage: 0.521E-2
  Auto-refine stage: 0.868E-3
 Adapative minimization will be done with:
  4 iterations in the exploratory stage
  5 iterations in the autorefine stage
To change these options see: www.perplex.ethz.ch/perplex_options.html

warning ver051 cannot make hmjL because of missing data or an invalid definition in the thermodynamic data file
…

** Starting auto_refine computational stage **
cycle   1   1   1
Initial number of divariant assemblages to be tested is: 1
Testing divariant assemblage   1,   0 assemblages remaining to be tested.
finished with equilibrium (1) di = br wo
finished with equilibrium (2) fo = br wo
warning ver047 univariant field   3 terminates at an invariant field that could not be located within the tolerance specified in the thermodynamic data file (PTOL= 0.300000E-02).
finished with equilibrium (3) br di = fo
warning ver020 sfol2
finished with equilibrium (3) br di = fo
finished with equilibrium (4) di = wo fo
Testing divariant assemblage   2,   1 assemblages remaining to be tested.
finished with equilibrium (5) q = wo
Testing divariant assemblage   3,   2 assemblages remaining to be tested.
finished with equilibrium (6) atg = di br
finished with equilibrium (3) fo = di br
warning ver047 univariant field   7 terminates at an invariant field that could not be located within the tolerance specified in the thermodynamic data file (PTOL= 0.300000E-02).
finished with equilibrium (7) atg = di fo
warning ver047 univariant field   7 terminates at an invariant field that could not be located within the tolerance specified in the thermodynamic data file (PTOL= 0.300000E-02).

finished with equilibrium (7) atg = di fo

warning ver047 univariant field   7 terminates at an invariant field that could not be located within the tolerance specified in the thermodynamic data file (PTOL= 0.300000E-02).

finished with equilibrium (7) atg = di fo

warning ver020 sfol2

finished with equilibrium (7) atg = di fo

warning ver047 univariant field   8 terminates at an invariant field that could not be located within the tolerance specified in the thermodynamic data file (PTOL= 0.300000E-02).

finished with equilibrium (8) br atg = fo

warning ver047 univariant field   8 terminates at an invariant field that could not be located within the tolerance specified in the thermodynamic data file (PTOL= 0.300000E-02).

finished with equilibrium (8) br atg = fo

warning ver047 univariant field   8 terminates at an invariant field that could not be located within the tolerance specified in the thermodynamic data file (PTOL= 0.300000E-02).

finished with equilibrium (8) br atg = fo

warning ver047 univariant field   8 terminates at an invariant field that could not be located within the tolerance specified in the thermodynamic data file (PTOL= 0.300000E-02).

finished with equilibrium (8) br atg = fo

warning ver020 sfol2

finished with equilibrium (8) br atg = fo

Testing divariant assemblage   4,   3 assemblages remaining to be tested.

finished with equilibrium (9) q tr = di

finished with equilibrium (10) q dol = di

finished with equilibrium (11) tr = di dol

finished with equilibrium (12) q dol = tr

finished with equilibrium (13) tr = di fo

finished with equilibrium (14) di dol = fo

warning ver047 univariant field   15 terminates at an invariant field that could not be located within the tolerance specified in the thermodynamic data file (PTOL= 0.300000E-02).

finished with equilibrium (15) tr dol = fo

warning ver047 univariant field   15 terminates at an invariant field that could not be located within the tolerance specified in the thermodynamic data file (PTOL= 0.300000E-02).

finished with equilibrium (15) tr dol = fo

warning ver047 univariant field   15 terminates at an invariant field that could not be located within the tolerance specified in the thermodynamic data file (PTOL= 0.300000E-02).

finished with equilibrium (15) tr dol = fo

warning ver047 univariant field   15 terminates at an invariant field that could not be located within the tolerance specified in the thermodynamic data file (PTOL= 0.300000E-02).

finished with equilibrium (15) tr dol = fo

warning ver020 sfol2

finished with equilibrium (15) tr dol = fo

finished with equilibrium (16) q ta = tr

finished with equilibrium (17) q dol = ta

warning ver047 univariant field   18 terminates at an invariant field that could not be located within the tolerance specified in the thermodynamic data file (PTOL= 0.300000E-02).

finished with equilibrium (18) ta = tr dol

finished with equilibrium (18) ta = tr dol

finished with equilibrium (19) tr = di atg

finished with equilibrium (7) atg = di fo

warning ver047 univariant field   20 terminates at an invariant field that could not be located within the tolerance specified in the thermodynamic data file (PTOL= 0.300000E-02).

finished with equilibrium (20) atg = tr fo

warning ver047 univariant field   20 terminates at an invariant field that could not be located within the tolerance specified in the thermodynamic data file (PTOL= 0.300000E-02).

finished with equilibrium (20) atg = tr fo

warning ver020 sfol2

finished with equilibrium (20) atg = tr fo

finished with equilibrium (21) tr dol = atg

finished with equilibrium (22) ta = tr atg

finished with equilibrium (23) dol ta = atg

finished with equilibrium (15) tr dol = fo

finished with equilibrium (24) dol atg = fo

warning ver074 no new equilibria identified, if degenerate segments have been skipped increase the computational reliability level.

finished with equilibrium (25) dol = br

finished with equilibrium (25) dol = br

warning ver066 Metastable assemblage into FLIPIT:
      di   q
v = 1000.00   873.000   0.267547E-01 0.00000   0.00000

Testing divariant assemblage   5,   3 assemblages remaining to be tested.
Testing divariant assemblage   6,   2 assemblages remaining to be tested.
Testing divariant assemblage   7,   2 assemblages remaining to be tested.
Testing divariant assemblage   8,   3 assemblages remaining to be tested.
Testing divariant assemblage   9,   3 assemblages remaining to be tested.
Testing divariant assemblage   10,   3 assemblages remaining to be tested.
Testing divariant assemblage   11,   2 assemblages remaining to be tested.
Testing divariant assemblage   12,   3 assemblages remaining to be tested.
Testing divariant assemblage   13,   3 assemblages remaining to be tested.
Testing divariant assemblage   14,   2 assemblages remaining to be tested.

warning ver066 Metastable assemblage into FLIPIT:
      ta   atg
v = 1000.00   573.000   0.781364E-02 0.00000   0.00000

Testing divariant assemblage   15,   1 assemblages remaining to be tested.
Testing divariant assemblage   16,   0 assemblages remaining to be tested.
Testing divariant assemblage   17,   0 assemblages remaining to be tested.
Testing divariant assemblage   18,   1 assemblages remaining to be tested.
Testing divariant assemblage   19,   1 assemblages remaining to be tested.
Testing divariant assemblage   20,   0 assemblages remaining to be tested.

(3) Plotting the calculated phase diagram (PSVDRAW)

Run PSVDRAW to plot the calculated phase diagram:

C:\PERPLEX\Perplex686>psvdraw

Perple_X version 6.8.6, source updated Jan 24, 2019.
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Enter the project or plot file name [i.e., without the .plt suffix]:
Ex5_1

Perple_X plot options are currently set as:

```
  Keyword:          Value:    Permitted values [default]:
  axis_label_scale      1.20      [1.2] (rel)
  bounding_box :
                    0     [0] x-min (pts)
                    0     [0] y-min (pts)
                  800     [800] x-length (pts)
                  800     [800] y-length (pts)
  field_fill        T       [T] F
  field_label       T       [T] F
  field_label_scale     0.75      [0.72] (rel)
  font              Helvetica
  grid              F       [F] T
  half_ticks        T       [T] F
  line_width        1.00      0-99 [1.] (pts)
  picture_transformation :
                  0.180    [0.18] x-scale (rel)
                  0.180    [0.18] y-scale (rel)
                  130.     [0.18] x-translation (pts)
                  220.     [0.18] y-translation (pts)
                  0.00     [0.0]  rotation (deg)
  plot_aspect_ratio     1.000     [1.0] x_axis_length/y_axis_length
  replicate_label       0.250     0->1 [0.025]
  splines           T       [T] F
  tenth_ticks       F       [F] T
  text_scale        1.000     [1.] (rel)
```
To change these options edit or create the plot option file
See: www.perplex.ethz.ch/perplex_plot_options.html

PostScript will be written to file: ex5_1.ps

Modify the default plot (y/n)?
y

Modify drafting options (y/n)?
 answer yes to modify:
  - x-y plotting limits
  - axes numbering
y

Modify x-y limits (y/n)?
n

Restrict phase fields by variance (y/n)?
 answer yes to:
  - suppress pseudounivariant curves and/or pseudoinvariant points of a specified true variance.
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

To simplify, we will exclude all those reaction curves that involve brucite.

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

Show only with assemblage (y/n)?

n

Show only without phases (y/n)?

y

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

br

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

enter

Show only with phases (y/n)?

n

Modify default equilibrium labeling (y/n)?
 answer yes to:
  - modify/suppress [pseudo-] univariant curve labels
  - suppress [pseudo-] invariant point labels

y

Suppress curve labels (y/n)?

n

Change default labeling of curve segments (y/n)?

y

Suppress labels of pseudounivariant curves (y/n)?

n

Enter minimum fraction of the axes length that a curve must be to receive a text label (0-1):

1

Enter minimum fraction of the axes length that a curve must be to receive a numeric label (0-1.000):

0

Suppress point labels (y/n)?

n

Modify default axes numbering (y/n)?

y

Enter the starting value and interval for major tick marks on the X-axis (current values are: 0.00   0.200   )
Enter the new values:
0
0.2

Enter the starting value and interval for major tick marks on the Y-axis (current values are: 573.   60.0   )
Enter the new values:
573
100

(4) di = wo fo   (15) tr dol = fo
(5) q = wo   (16) q ta = tr
(7) atg = di fo   (17) q dol = ta
(9) q tr = di   (18) ta = tr dol
(10) q dol = di   (19) tr = di atg
(11) tr = di dol   (20) atg = tr fo
(12) q dol = tr   (21) tr dol = atg
(13) tr = di fo   (22) ta = tr atg
(14) di dol = fo   (23) dol ta = atg
                     (24) dol atg = fo
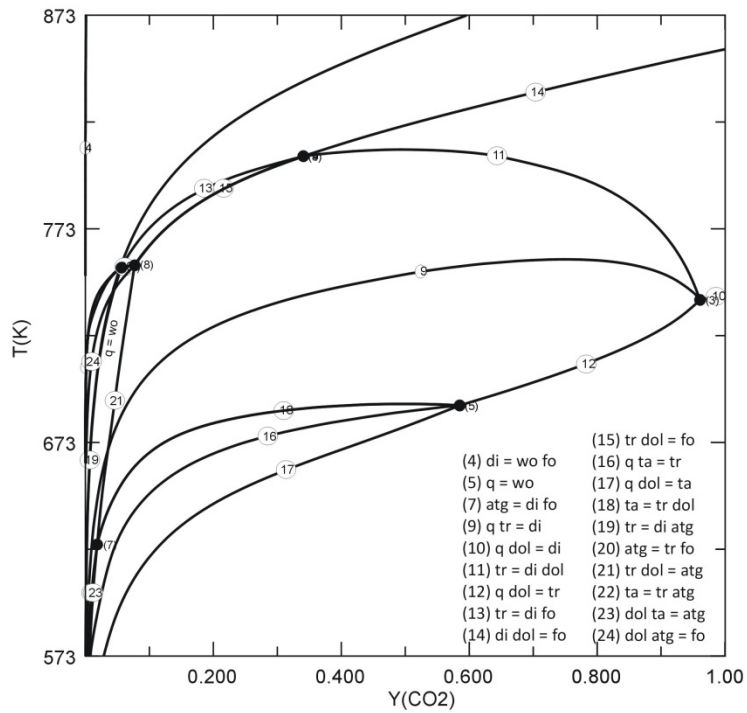
Ex. 5.2 – Isobaric T-XCO$_2$ pseudosection of a siliceous dolomite for the composition 2Qtz–2Dol–1Cal   (see Bucher & Grapes, 2011; Fig. 6.8)

(1) Definition of the problem (BUILD)

C:\PERPLEX\Perplex686>build

Perple_X version 6.8.6, source updated Jan 24, 2019.
Copyright (C) 1986-2019 James A D Connolly <www.perplex.ethz/copyright.html>.

NO is the default (blank) answer to all Y/N prompts

Enter a name for this project (the name will be used as the root for all output file names) [default = my_project]:
Ex5_2

The problem definition file will be named: ex5_2.dat

Enter thermodynamic data file name [default = hp02ver.dat]:
hp62ver.dat

Enter the computational option file name [default = perplex_option.dat]:
See: www.perplex.ethz.ch/perplex_options.html

Reading Perple_X options from: perplex_option.dat

The current data base components are:
 Na2O MgO Al2O3 SiO2 K2O   CaO   TiO2 MnO   FeO   NiO   ZrO2 Cl2   O2   H2O   CO2   CuO   Cr2O3 S2
F2
Transform them (Y/N)?
n

Specify computational mode:
    1 - Convex-Hull minimization
    2 - Constrained minimization on a 2d grid [default]
    3 - Constrained minimization on a 1d grid
    4 - Output pseudocompound data
    5 - 1-d Phase fractionation calculations
    6 - 0-d Infiltration-reactionation-fractionation
    7 - 2-d Phase fractionation (FRAC2D and TITRATE reactive transport models)
Use Convex-Hull minimization for Schreinemakers projections or phase diagrams with > 2 independent variables. Use constrained minimization for phase diagrams or phase diagram sections with < 3 independent variables.
2

Calculations with a saturated fluid (Y/N)?
y

Select the independent saturated fluid components:

 H2O   CO2

Enter names, 1 per line, press <enter> 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

Select thermodynamic components from the set:

 Na2O MgO   Al2O3 SiO2 K2O   CaO   TiO2 MnO   FeO   NiO ZrO2 Cl2 O2   CuO   Cr2O3 S2   F2

Enter names, 1 per line, press <enter> to finish:

MgO

CaO

SiO2

Because the thermodynamic data file identifies: H2O   CO2 as special components, you will be prompted next for the EoS to be used for the corresponding composants and mixtures thereof. To override this behavior, e.g., to use a generic hybrid fluid EoS, delete the special_component section from the thermodynamic data file header.

Select fluid equation of state:

  0 - X(CO2) H2O-CO2 Modified Redlich-Kwong (MRK) DeSantis et al 74

  1 - X(CO2) H2O-CO2 HSMRK Kerrick & Jacobs 81

  2 - X(CO2) H2O-CO2 MRK hybrid-EoS*

  5 - X(CO2) H2O-CO2 CORK Holland & Powell 91, 98

  8 - f(O2/CO2) C-buffered COH MRK hybrid-EoS*

 10 - X(O) C-buffered COH MRK hybrid-EoS Connolly & Cesare 93*

 12 - X(O)-f(S2) C-buffered COHS MRK hybrid-EoS Connolly & Cesare 93*

 13 - X(H2) H2O-H2 MRK hybrid-EoS*

 14 - X(CO2) H2O-CO2 Pitzer & Sterner 94; Holland & Powell mixing 03

 15 - X(H2) H2O-H2 low T MRK hybrid-EoS*

 16 - X(O) H-O MRK hybrid-EoS*

 17 - X(O)-f(S2) H-O-S MRK hybrid-EoS*

 19 - X(O)-X(S) C-buffered COHS MRK hybrid-EoS Connolly & Cesare 93*

 20 - X(O)-X(C) COHS MRK hybrid-EoS Connolly & Cesare 93*

 24 - f(O2/CO2)-N/C C-buffered COHN MRK hybrid-EoS*

 25 - X(CO2)-X(NaCl) H2O-CO2-NaCl Aranovich et al 10

 26 - X(O) O-Si MRK Connolly 16

 27 - X(O)-X(C) C-O-H MRK hybrid-EoS*

*Hybrid EoS use the following pure species EoS, to change these associations modify the hybrid_EoS keywords in the perplex_option file:

    H2O - PSEoS Pitzer & Sterner 1994

    CO2 - PSEoS Pitzer & Sterner 1994

    CH4 - HSMRK Kerrick & Jacobs 1981

5

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

Select x-axis variable:
    1 - P(bar)
    2 - T(K)
    3 - Y(CO2)
    4 - Composition X_C1* (user defined)
*X_C1 can not be selected as the y-axis variable
3

Enter minimum and maximum values, respectively, for: Y(CO2)
0
1

Select y-axis variable:
    2 - T(K)
    3 - P(bar)
2

Enter minimum and maximum values, respectively, for: T(K)
573
873

Specify sectioning value for: P(bar)
1000

For gridded minimization, grid resolution is determined by the number of levels (grid_levels) and the resolution at the lowest level in the X- and Y-directions (x_nodes and y_nodes) these parameters are currently set for the exploratory and autorefi ne cycles as follows:

stage	grid_levels	xnodes	ynodes	effective resolution
exploratory	1	60	60	60 x 60 nodes
auto-refine	4	60	60	473 x 473 nodes

To change these options edit or create the file perplex_option.dat
See: www.perplex.ethz.ch/perplex_options.html#grid_parameters

Specify component amounts by mass (Y/N)?
n

The amounts you enter next need not be normalized; regardless of units, they define the molar amount of the system
The starting composition 2Qtz +2Dol + 1Cal means: 2SiO2 + 2MgO + 3CaO

Enter the molar amounts of the components:
 MgO CaO SiO2
for the bulk composition of interest:
2

3
2

Output a print file (Y/N)?
y

warning ver051 cannot make hmjL   because of missing data or an invalid definition in the thermodynamic data file.
…

Exclude pure and/or endmember phases (Y/N)?
y
Do you want to be prompted for phases (Y/N)?
n
Enter names, 1 per line, press <enter> to finish:
cumm_dqf
fo8L
q8L
cenjh
odi
qjL
dijL
fojL
foTL
mcpv
cmpv
foHL
qHL
lrn
spu
merw
ty
mont
rnk
ak
cen

Include solution models (Y/N)?
n

Enter calculation title:
Ex5_2

(2) Doing the calculation (VERTEX)

Run VERTEX to make the calculation:

C:\PERPLEX\Perplex686>vertex

Perple_X version 6.8.6, source updated Jan 24, 2019.
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Enter the project name (the name assigned in BUILD) [default = my_project]:
Ex5_2

Reading problem definition from file: ex5_2.dat
Reading thermodynamic data from file: hp62ver.dat
Reading solution models from file: not requested
Writing print output to file: ex5_2.prn
Writing plot output to file: ex5_2.plt
Writing bulk composition plot output to file: ex5_2.blk
Reading Perple_X options from: perplex_option.dat
Writing Perple_X option summary to file: not requested

Perple_X version 6.8.6, source updated Jan 24, 2019.
Copyright (C) 1986-2019 James A D Connolly <www.perplex.ethz/copyright.html>.

Perple_X computational option settings for VERTEX:
   Keyword: Value: Permitted values [default]:
  Auto-refine options:
   auto_refine   man   off manual [auto]
  Free energy minimization options:
   final_resolution:
     exploratory stage   0.1E-1   [1e-2], target value, see actual values be low
     auto-refine stage   0.1E-2   [1e-3], target value, see actual values be low
   resolution_factor   2   >= 2 [2]
   refinement_points   5   [aut] or 1->12; aut = automatic
   solvus_tolerance_II   aut   0->1 [0.2]
   global_reach_increment 0   >= 0 [0]
   reach_increment_switch on   [on] off all
   zero_mode   0.1E-05   0->1 [1e-6]; < 0 => off
  2D grid options:

   x_nodes   40 / 40   [20/40], >0, <2048; effective x-resolution
  60 / 473 nodes
   y_nodes   40 / 40   [20/40], >0, <2048; effective y-resolution
  60 / 473 nodes
   grid_levels   1 / 4   [1/4], >0, <10
   linear_model   on   off [on]
  Solution subdivision options:
   initial_resolution:
     exploratory stage   0.0625   0->1 [1/16], 0 => off
     auto-refine stage   0.0208   0->1 [1/48], 0 => off
   stretch_factor   0.0020   >0 [2d-3]

```
subdivision_override   off      [off] lin str
hard_limits           off      [off] on
refine_endmembers     F        [F] T
Thermodynamic options:
solvus_tolerance      aut      [aut] or 0->1; aut = automatic, 0 => p=c pseudocompounds, 1 => homogenize
T_stop (K)            0.0      [0]
T_melt (K)            873.0    [873]
order_check           on       off [on]
approx_alpha          T        [T] F
Anderson-Gruneisen    F        [F] T
speciation_factor     100.     >10 [100] speciation precision = final resolution/speciation_factor
speciation_max_it     100      [100]
hybrid_EoS_H2O        4        [4] 0-2, 4-7
hybrid_EoS_CO2        4        [4] 0-4, 7
hybrid_EoS_CH4        0        [0] 0-1, 7
aq_bad_results        err      [err] 101, 102, 103, ignore
aq_lagged_speciation  F        [F] T
aq_ion_H+             T        [T] F => use OH-
aq_oxide_components   F        [F] T
aq_solvent_solvus     T        [T] F
aq_vapor_epsilon      1.0      [1.]
Input/Output options:
dependent_potentials  off      off [on]
pause_on_error        T        [T] F
auto_exclude          T        [T] F
logarithmic_p         F        [F] T
bad_number            NaN      [NaN]
interim_results       aut      [auto] off manual
Information file output options:
option_list_files     F        [F] T; echo computational options
pseudocompound_file   F        [F] T; echo static pseudocompound compositions
auto_refine_file      F        [F] T; echo auto-refine compositions
Worst case (Cartesian) compositional resolution (mol):
Exploratory stage:   0.521E-2
Auto-refine stage:   0.868E-3
Adapative minimization will be done with:
4 iterations in the exploratory stage
5 iterations in the autorefine stage
To change these options see: www.perplex.ethz.ch/perplex_options.html
…


** Starting auto_refine computational stage **
0.3% done with low level grid.
2.9% done with low level grid.
5.4% done with low level grid.
8.0% done with low level grid.
10.5% done with low level grid.
13.1% done with low level grid.
15.7% done with low level grid.
18.2% done with low level grid.
20.8% done with low level grid.
```

23.3% done with low level grid.
25.9% done with low level grid.
28.4% done with low level grid.
31.0% done with low level grid.
33.5% done with low level grid.
36.1% done with low level grid.
38.7% done with low level grid.
41.2% done with low level grid.
43.8% done with low level grid.
46.3% done with low level grid.
48.9% done with low level grid.
51.4% done with low level grid.
54.0% done with low level grid.
56.5% done with low level grid.
59.1% done with low level grid.
61.7% done with low level grid.
64.2% done with low level grid.
66.8% done with low level grid.
69.3% done with low level grid.
71.9% done with low level grid.
74.4% done with low level grid.
77.0% done with low level grid.
79.6% done with low level grid.
82.1% done with low level grid.
84.7% done with low level grid.
87.2% done with low level grid.
89.8% done with low level grid.
92.3% done with low level grid.
94.9% done with low level grid.
97.4% done with low level grid.
100.0% done with low level grid.

Beginning grid refinement stage.
   234 grid cells to be refined at grid level 2
      ...working (502 minimizations done)
      refinement at level 2 involved   534 minimizations
  2134 minimizations required of the theoretical limit of   6241
   461 grid cells to be refined at grid level 3
      ...working (470 minimizations done)
      ...working (971 minimizations done)
      refinement at level 3 involved   975 minimizations
  3109 minimizations required of the theoretical limit of   24649
   916 grid cells to be refined at grid level 4
      ...working (498 minimizations done)
      ...working (1000 minimizations done)
      ...working (1501 minimizations done)
      refinement at level 4 involved   1893 minimizations
  5002 minimizations required of the theoretical limit of   98596

(3) Plotting the calculated phase diagram (PSSECT)

Run PSSECT to plot the calculated pseudosection:

C:\PERPLEX\Perplex686>pssect

Perple_X version 6.8.6, source updated Jan 24, 2019.
Copyright (C) 1986-2019 James A D Connolly <www.perplex.ethz/copyright.html>.

Enter the project name (the name assigned in BUILD) [default = my_project]:
Ex5_2

Reading Perple_X options from: perplex_option.dat

Perple_X plot options are currently set as:
  Keyword: Value: Permitted values [default]:
  axis_label_scale   1.20   [1.2] (rel)
  bounding_box :
                    0   [0] x-min (pts)
                    0   [0] y-min (pts)
                  800   [800] x-length (pts)
                  800   [800] y-length (pts)
  field_fill   T   [T] F
  field_label   T   [T] F
  field_label_scale   0.75   [0.72] (rel)
  font   Helvetica
  grid   F   [F] T
  half_ticks   T   [T] F
  line_width   1.00   0-99 [1.] (pts)
  picture_transformation :
                  0.180   [0.18] x-scale (rel)
                  0.180   [0.18] y-scale (rel)
                  130.   [0.18] x-translation (pts)
                  220.   [0.18] y-translation (pts)
                  0.00   [0.0] rotation (deg)
  plot_aspect_ratio   1.000   [1.0] x_axis_length/y_axis_length
  replicate_label   0.250   0->1 [0.025]
  splines   T   [T] F
  tenth_ticks   F   [F] T
  text_scale   1.000   [1.] (rel)
To change these options edit or create the plot option file
See: www.perplex.ethz.ch/perplex_plot_options.html

PostScript will be written to file: ex5_2.ps

Modify the default plot (y/n)?
N
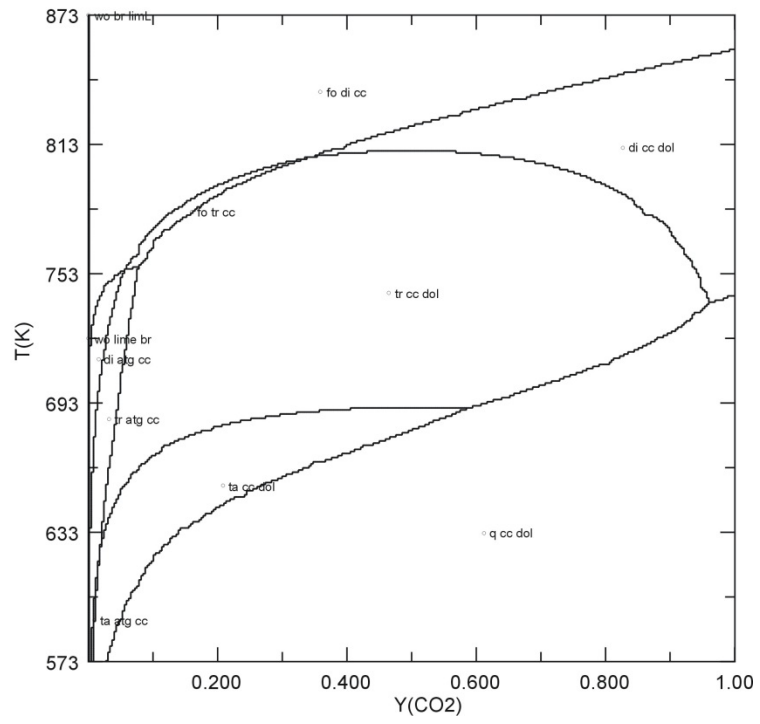
Ex. 5.3 – Isobaric T-X(CO₂) projection for a generic siliceous limestone containing excess Qtz

(1) Definition of the problem (BUILD)

The problem is the same as in Ex. 5.1, except for the choice of the excess component that is now SiO2 (quartz is in excess). **You can edit the ex5_1.dat input file** (change the name in ex5_3). The thermodynamic components are now MgO and CaO, whereas the saturated component is SiO2.

```
begin thermodynamic component list
MgO  0 0.00000    0.00000    0.00000    unconstrained amount
CaO  0 0.00000    0.00000    0.00000    unconstrained amount
end thermodynamic component list

begin saturated component list
SiO2  0 0.00000    0.00000    0.00000    unconstrained amount
end saturated component list
```

(2) Doing the calculation (CONVEX)

Run CONVEX to make the calculation:

C:\PERPLEX\Perplex686>convex

Perple_X version 6.8.6, source updated Jan 24, 2019.
Copyright (C) 1986-2019 James A D Connolly <www.perplex.ethz/copyright.html>.

Enter the project name (the name assigned in BUILD) [default = my_project]:
Ex5_3

Reading problem definition from file: ex5_3.dat
Reading thermodynamic data from file: hp62ver.dat
Reading solution models from file: not requested
Writing print output to file: ex5_3.prn
Writing plot output to file: ex5_3.plt
Reading Perple_X options from: perplex_option.dat
Writing complete reaction list to file: not requested
Writing Perple_X option summary to file: not requested

Perple_X version 6.8.6, source updated Jan 24, 2019.
Copyright (C) 1986-2019 James A D Connolly <www.perplex.ethz/copyright.html>.

Perple_X computational option settings for CONVEX:
   Keyword: Value: Permitted values [default]:
  Auto-refine options:
   auto_refine   man   off manual [auto]
  Schreinemakers and Mixed-variable diagram options:
   variance   1 /99   [1/99], >0, maximum true variance
   increment   0.100/0.025   [0.1/0.025], default search/trace variable
  increment

```
     efficiency          3      [3] >0 < 6
     reaction_format     min     [min] full stoichiometry S+V everything
     reaction_list       off     [off] on
     console_messages    on      [on] off
     short_print_file    on      [on] off
   Solution subdivision options:
    initial_resolution:
     exploratory stage   0.0625    0->1 [1/16], 0 => off
     auto-refine stage   0.0208    0->1 [1/48 ], 0 => off
    stretch_factor       0.0020    >0 [2d-3]
    subdivision_override  off     [off] lin str
    hard_limits          off     [off] on
    refine_endmembers    F       [F] T
    pc_perturbation      0.0050    [5d-3]
   Thermodynamic options:
    solvus_tolerance     aut     [aut] or 0->1; aut = automatic, 0 => p=c pseudocompounds, 1 => homogenize
    T_stop (K)           0.0     [0]
    T_melt (K)           873.0    [873]
    order_check          on      off [on]
    approx_alpha         T       [T] F
    Anderson-Gruneisen   F       [F] T
    speciation_factor    100.    >10 [100] speciation precision = final resolution/speciation_factor
    speciation_max_it    100     [100]
    hybrid_EoS_H2O       4       [4] 0-2, 4-7
    hybrid_EoS_CO2       4       [4] 0-4, 7
    hybrid_EoS_CH4       0       [0] 0-1, 7
    aq_bad_results       err     [err] 101, 102, 103, ignore
    aq_lagged_speciation  F      [F] T
    aq_ion_H+            T       [T] F => use OH-
    aq_oxide_components  F       [F] T
    aq_solvent_solvus    T       [T] F
    aq_vapor_epsilon     1.0     [1.]
   Input/Output options:
    dependent_potentials  off    off [on]
    pause_on_error       T       [T] F
    auto_exclude         T       [T] F
   Worst case (Cartesian) compositional resolution (mol):
    Exploratory stage:   0.521E-2
    Auto-refine stage:   0.868E-3
   Adapative minimization will be done with:
     4 iterations in the exploratory stage
     5 iterations in the autorefine stage
To change these options see: www.perplex.ethz.ch/perplex_options.html
…


** Starting auto_refine computational stage **
cycle       1      1      1
 cycle      2      2      2
 cycle      3      3      3
Initial number of divariant assemblages to be tested is:    3
Testing divariant assemblage    1,    2 assemblages remaining to be tested.
```

finished with equilibrium (1) ta cc = tr
finished with equilibrium (2) ta dol = tr
finished with equilibrium (3) dol = ta cc
finished with equilibrium (4) dol = tr cc
finished with equilibrium (5) mag = ta
finished with equilibrium (5) mag = ta
finished with equilibrium (6) dol mag = tr
finished with equilibrium (7) tr cc = di
warning ver047 univariant field   8 terminates at an invariant field that could not be located within the tolerance specified in the thermodynamic data file (PTOL= 0.300000E-02).
finished with equilibrium (8) dol = di
warning ver020 sfol2
finished with equilibrium (8) dol = di
finished with equilibrium (8) dol = di
finished with equilibrium (9) ta = en
finished with equilibrium (10) mag = en
finished with equilibrium (11) dol en = tr
finished with equilibrium (10) mag = en
finished with equilibrium (10) mag = en
finished with equilibrium (12) ta = anth
finished with equilibrium (13) anth = en
finished with equilibrium (8) dol = di
finished with equilibrium (14) tr = en di
finished with equilibrium (8) dol = di
Testing divariant assemblage   2,   2 assemblages remaining to be tested.
Testing divariant assemblage   3,   2 assemblages remaining to be tested.
finished with equilibrium (15) cc = wo
Testing divariant assemblage   4,   2 assemblages remaining to be tested.
Testing divariant assemblage   5,   3 assemblages remaining to be tested.
Testing divariant assemblage   6,   3 assemblages remaining to be tested.
Testing divariant assemblage   7,   2 assemblages remaining to be tested.
Testing divariant assemblage   8,   2 assemblages remaining to be tested.
Testing divariant assemblage   9,   2 assemblages remaining to be tested.
Testing divariant assemblage   10,   3 assemblages remaining to be tested.
Testing divariant assemblage   11,   3 assemblages remaining to be tested.
Testing divariant assemblage   12,   3 assemblages remaining to be tested.
Testing divariant assemblage   13,   3 assemblages remaining to be tested.
Testing divariant assemblage   14,   3 assemblages remaining to be tested.
Testing divariant assemblage   15,   2 assemblages remaining to be tested.
Testing divariant assemblage   16,   2 assemblages remaining to be tested.
Testing divariant assemblage   17,   1 assemblages remaining to be tested.
Testing divariant assemblage   18,   0 assemblages remaining to be tested.
Testing divariant assemblage   19,   1 assemblages remaining to be tested.
Testing divariant assemblage   20,   0 assemblages remaining to be tested.
Testing divariant assemblage   21,   0 assemblages remaining to be tested.
Testing divariant assemblage   22,   0 assemblages remaining to be tested.

(3) Plotting the calculated phase diagram (PSVDRAW)

Run PSVDRAW to plot the calculated phase diagram:

C:\PERPLEX\Perplex686>psvdraw

Perple_X version 6.8.6, source updated Jan 24, 2019.
Copyright (C) 1986-2019 James A D Connolly <www.perplex.ethz/copyright.html>.

Enter the project or plot file name [i.e., without the .plt suffix]:
Ex5_3

Perple_X plot options are currently set as:
    Keyword: Value: Permitted values [default]:
    axis_label_scale   1.20   [1.2] (rel)
    bounding_box :
                    0   [0] x-min (pts)
                    0   [0] y-min (pts)
                  800   [800] x-length (pts)
                  800   [800] y-length (pts)
    field_fill   T   [T] F
    field_label   T   [T] F
    field_label_scale   0.75   [0.72] (rel)
    font   Helvetica
    grid   F   [F] T
    half_ticks   T   [T] F
    line_width   1.00   0-99 [1.] (pts)
    picture_transformation :
                  0.180   [0.18] x-scale (rel)
                  0.180   [0.18] y-scale (rel)
                  130.   [0.18] x-translation (pts)
                  220.   [0.18] y-translation (pts)
                  0.00   [0.0] rotation (deg)
    plot_aspect_ratio   1.000   [1.0] x_axis_length/y_axis_length
    replicate_label   0.250   0->1 [0.025]
    splines   T   [T] F
    tenth_ticks   F   [F] T
    text_scale   1.000   [1.] (rel)
To change these options edit or create the plot option file
See: www.perplex.ethz.ch/perplex_plot_options.html

PostScript will be written to file: ex4_3.ps

Modify the default plot (y/n)?
n
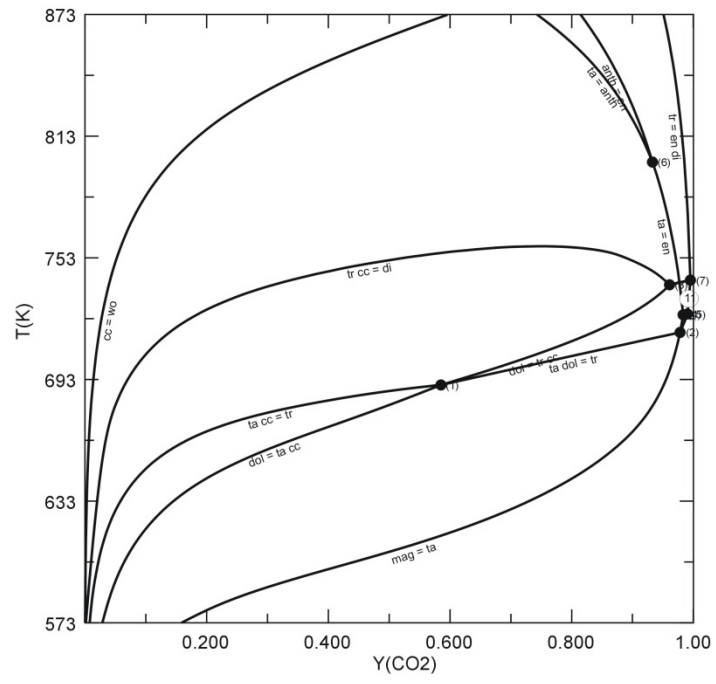
Ex. 5.4 – Isobaric T-XCO$_2$ pseudosection of a siliceous limestone for the composition 6Qtz–2Dol–1Cal (see Bucher & Grapes, 2011; Fig. 6.12)

(1) Definition of the problem (BUILD)

The problem is the same as in Ex. 5.2, except for the composition of the system that is now 6Qtz + 2Dol + 1Cal, corresponding to 6SiO2 + 2MgO + 3CaO. **You can edit the ex5_2.dat input file** (change the name in ex5_4) (see below).

begin thermodynamic component list
MgO 1 2.00000   0.00000   0.00000   molar amount
CaO 1 3.00000   0.00000   0.00000   molar amount
SiO2 1 6.00000   0.00000   0.00000   molar amount
end thermodynamic component list

(2) Doing the calculation (VERTEX)

Run VERTEX to make the calculation:

C:\PERPLEX\Perplex686>vertex

Perple_X version 6.8.6, source updated Jan 24, 2019.
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Enter the project name (the name assigned in BUILD) [default = my_project]:
Ex5_4

Reading problem definition from file: ex5_4.dat
Reading thermodynamic data from file: hp62ver.dat
Reading solution models from file: not requested
Writing print output to file: ex5_4.prn
Writing plot output to file: ex5_4.plt
Writing bulk composition plot output to file: ex5_4.blk
Reading Perple_X options from: perplex_option.dat
Writing Perple_X option summary to file: not requested

Perple_X version 6.8.6, source updated Jan 24, 2019.
Copyright (C) 1986-2019 James A D Connolly <www.perplex.ethz/copyright.html>.

Perple_X computational option settings for VERTEX:
   Keyword: Value: Permitted values [default]:
  Auto-refine options:
    auto_refine   man   off manual [auto]
  Free energy minimization options:
   final_resolution:
     exploratory stage   0.1E-1   [1e-2], target value, see actual values be low
     auto-refine stage   0.1E-2   [1e-3], target value, see actual values be low
    resolution_factor   2   >= 2 [2]
    refinement_points   5   [aut] or 1->12; aut = automatic

solvus_tolerance_II   aut   0->1 [0.2]
global_reach_increment 0   >= 0 [0]
reach_increment_switch on   [on] off all
zero_mode   0.1E-05   0->1 [1e-6]; < 0 => off
2D grid options:
 x_nodes   40 / 40   [20/40], >0, <2048; effective x-resolution   40 / 313 nodes
 y_nodes   40 / 40   [20/40], >0, <2048; effective y-resolution   40 / 313 nodes
 grid_levels   1 / 4   [1/4], >0, <10
 linear_model   on   off [on]
Solution subdivision options:
 initial_resolution:
   exploratory stage   0.0625   0->1 [1/16], 0 => off
   auto-refine stage   0.0208   0->1 [1/48], 0 => off
 stretch_factor   0.0020   >0 [2d-3]
 subdivision_override   off   [off] lin str
 hard_limits   off   [off] on
 refine_endmembers   F   [F] T
Thermodynamic options:
 solvus_tolerance   aut   [aut] or 0->1; aut = automatic, 0 => p=c pseudocompounds, 1 => homogenize
 T_stop (K)   0.0   [0]
 T_melt (K)   873.0   [873]
 order_check   on   off [on]
 approx_alpha   T   [T] F
 Anderson-Gruneisen   F   [F] T
 speciation_factor   100.   >10 [100] speciation precision = final resolution/speciation_factor
 speciation_max_it   100   [100]
 hybrid_EoS_H2O   4   [4] 0-2, 4-7
 hybrid_EoS_CO2   4   [4] 0-4, 7
 hybrid_EoS_CH4   0   [0] 0-1, 7
 aq_bad_results   err   [err] 101, 102, 103, ignore
 aq_lagged_speciation F   [F] T
 aq_ion_H+   T   [T] F => use OH-
 aq_oxide_components   F   [F] T
 aq_solvent_solvus   T   [T] F
 aq_vapor_epsilon   1.0   [1.]
Input/Output options:
 dependent_potentials   off   off [on]
 pause_on_error   T   [T] F
 auto_exclude   T   [T] F
 logarithmic_p   F   [F] T
 bad_number   NaN   [NaN]
 interim_results   aut   [auto] off manual
Information file output options:
 option_list_files   F   [F] T; echo computational options
 pseudocompound_file   F   [F] T; echo static pseudocompound compositions
 auto_refine_file   F   [F] T; echo auto-refine compositions
Worst case (Cartesian) compositional resolution (mol):
 Exploratory stage: 0.521E-2
 Auto-refine stage: 0.868E-3
Adapative minimization will be done with:
 4 iterations in the exploratory stage

5 iterations in the autorefine stage
To change these options see: www.perplex.ethz.ch/perplex_options.html

…

** Starting auto_refine computational stage **
0.3% done with low level grid.
 2.9% done with low level grid.
 5.4% done with low level grid.
 8.0% done with low level grid.
10.5% done with low level grid.
13.1% done with low level grid.
15.7% done with low level grid.
18.2% done with low level grid.
20.8% done with low level grid.
23.3% done with low level grid.
25.9% done with low level grid.
28.4% done with low level grid.
31.0% done with low level grid.
33.5% done with low level grid.
36.1% done with low level grid.
38.7% done with low level grid.
41.2% done with low level grid.
43.8% done with low level grid.
46.3% done with low level grid.
48.9% done with low level grid.
51.4% done with low level grid.
54.0% done with low level grid.
56.5% done with low level grid.
59.1% done with low level grid.
61.7% done with low level grid.
64.2% done with low level grid.
66.8% done with low level grid.
69.3% done with low level grid.
71.9% done with low level grid.
74.4% done with low level grid.
77.0% done with low level grid.
79.6% done with low level grid.
82.1% done with low level grid.
84.7% done with low level grid.
87.2% done with low level grid.
89.8% done with low level grid.
92.3% done with low level grid.
94.9% done with low level grid.
97.4% done with low level grid.
100.0% done with low level grid.

Beginning grid refinement stage.
  204 grid cells to be refined at grid level 2
     refinement at level 2 involved   436 minimizations
 2036 minimizations required of the theoretical limit of   6241
  366 grid cells to be refined at grid level 3

```
    ...working (    66 minimizations done)
    ...working (   567 minimizations done)
    refinement at level 3 involved    705 minimizations
2741 minimizations required of the theoretical limit of   24649
 682 grid cells to be refined at grid level 4
    ...working (   363 minimizations done)
    ...working (   864 minimizations done)
    refinement at level 4 involved   1270 minimizations
4011 minimizations required of the theoretical limit of   98596
```

(3) Plotting the calculated phase diagram (PSSECT)

Run PSSECT to plot the calculated pseudosection:

C:\PERPLEX\Perplex686>pssect

Perple_X version 6.8.6, source updated Jan 24, 2019.
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Enter the project name (the name assigned in BUILD) [default = my_project]:
Ex5_4

Reading Perple_X options from: perplex_option.dat
Perple_X plot options are currently set as:
   Keyword: Value: Permitted values [default]:
   axis_label_scale   1.20   [1.2] (rel)
   bounding_box :
                  0   [0] x-min (pts)
                  0   [0] y-min (pts)
                800   [800] x-length (pts)
                800   [800] y-length (pts)
   field_fill   T   [T] F
   field_label   T   [T] F
   field_label_scale   0.75   [0.72] (rel)
   font   Helvetica
   grid   F   [F] T
   half_ticks   T   [T] F
   line_width   1.00   0-99 [1.] (pts)
   picture_transformation :
                0.180   [0.18] x-scale (rel)
                0.180   [0.18] y-scale (rel)
                130.   [0.18] x-translation (pts)
                220.   [0.18] y-translation (pts)
                0.00   [0.0] rotation (deg)
   plot_aspect_ratio   1.000   [1.0] x_axis_length/y_axis_length
   replicate_label   0.250   0->1 [0.025]
   splines   T   [T] F
   tenth_ticks   F   [F] T
   text_scale   1.000   [1.] (rel)
To change these options edit or create the plot option file
```

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

PostScript will be written to file: ex5_4.ps

Modify the default plot (y/n)?

n

Comparison between the isobaric T-X(CO₂) projection for a generic siliceous dolomite containing excess calcite (Ex. 5.1) and the pseudosection calculated for a bulk composition MgO=2, CaO=3, SiO2=2 mol% (2Qtz+2Dol+1Cal; Ex. 5.2). **This specific bulk composition "sees" (i.e. is sensible to) only some of the reactions predicted by the P-T projection.**

The reaction list in the left figure:

(4) di = wo fo    (15) tr dol = fo
(5) q = wo        (16) q ta = tr
(7) atg = di fo   (17) q dol = ta
(9) q tr = di     (18) ta = tr dol
(10) q dol = di   (19) tr = di atg
(11) tr = di dol  (20) atg = tr fo
(12) q dol = tr   (21) tr dol = atg
(13) tr = di fo   (22) ta = tr atg
(14) di dol = fo  (23) dol ta = atg
                  (24) dol atg = fo



Comparison between the isobaric T-X(CO2) projection for a generic siliceous limestone containing excess quarz (Ex. 5.3) and the pseudosection calculated for a bulk composition MgO=2%, CaO=3, SiO2=6 mol% (6Qtz+2Dol+1Cal; Ex. 5.4). **This specific bulk composition "sees" (i.e. is sensible to) only some of the reactions predicted by the P-T projection.**

# Ex. 6

# Ex. 6 – T-XMg section for the CaCO₃-MgCO₃ system (*solvus* relations)

**This exercise explains how to calculate *solvus* relations in the system CaCO$_3$-MgCO$_3$.** In this system two miscibility gaps exist, and the phases on either side of the gaps are calcite/dolomite, and dolomite/magnesite, respectively. The amounts of MgCO$_3$ in calcite in equilibrium with dolomite, and that of CaCO$_3$ in magnesite in equilibrium with dolomite, change as a function of temperature, and can be used as geothermometers. The effect of pressure on the Cal-Dol and Dol-Mag *solvi* is investigated by calculating the same phase diagram at different pressures.

---

**The issue can be treated as a simple isobaric T-X pseudosection, where X (XMg) varies between 0 (XMg=0; Cal) and 1 (XMg=1; Mag). Opposite to Ex. 4 and 5, <u>solid solutions must now be considered</u>. Perplex deals with solid solutions by creating a whole set of "pseudocompounds" (intermediate compositions), and treating each of them like a separate phase.** Thus, if a carbonate with composition Cal$_{90}$ has a lower free energy than Cal$_{95}$ at a particular P-T condition, Cal$_{90}$ will be considered as the stable carbonate.

---

Pseudocompounds are indicated with abbreviations, whose meaning is sometimes not immediately understandable. To understand the meaning of these abbreviations, **I suggest changing to T (true) the default value of the pseudocompound_file keyword in the perplex_option.dat file.** Doing in this way, VERTEX will create an additional output file, listing the composition of each pseudocompound.

## (1) Definition of the problem (BUILD)

C:\PERPLEX\Perplex686>build

Perple_X version 6.8.6, source updated Jan 24, 2019.
Copyright (C) 1986-2019 James A D Connolly <www.perplex.ethz/copyright.html>.

NO is the default (blank) answer to all Y/N prompts

Enter a name for this project (the name will be used as the root for all output file names) [default = my_project]:
ex6_5kbar

The problem definition file will be named: ex6_5kbar.dat

Enter thermodynamic data file name [default = hp02ver.dat]:
hp62ver.dat

Enter the computational option file name [default = perplex_option.dat]:
See: www.perplex.ethz.ch/perplex_options.html

Reading Perple_X options from: perplex_option.dat

The current data base components are:

Na2O  MgO  Al2O3 SiO2 K2O  CaO  TiO2 MnO  FeO  NiO  ZrO2 Cl2 O2   H2O  CO2  CuO  Cr2O3 S2
F2

Transform them (Y/N)?

n

Specify computational mode:

    1 - Convex-Hull minimization

    2 - Constrained minimization on a 2d grid [default]

    3 - Constrained minimization on a 1d grid

    4 - Output pseudocompound data

    5 - 1-d Phase fractionation calculations

    6 - 0-d Infiltration-reactionation-fractionation

    7 - 2-d Phase fractionation (FRAC2D and TITRATE reactive transport models)

Use Convex-Hull minimization for Schreinemakers projections or phase diagrams with > 2 independent variables. Use constrained minimization for phase diagrams or phase diagram sections with < 3 independent variables.

The problem can be treated as an isobaric T-X pseudosection, where X varies between 0 (XMg=0; Cal) and 1 (XMg=1; Mag).

2

Calculations with a saturated fluid (Y/N)?

y

Select the independent saturated fluid components:

 H2O   CO2

Enter names, 1 per line, press <enter> 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.

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   H2O  CuO  Cr2O3 S2   F2

Enter names, 1 per line, press <enter> to finish:

MgO

CaO

Because the thermodynamic data file identifies: CO2 as special components, you will be prompted next for the EoS to be used for the corresponding composants and mixtures thereof. To override this behavior,e.g., to use a generic hybrid fluid EoS, delete the special_component section from the thermodynamic data file header.

Select fluid equation of state:

---

0 - X(CO2) H2O-CO2 Modified Redlich-Kwong (MRK) DeSantis et al 74

1 - X(CO2) H2O-CO2 HSMRK Kerrick & Jacobs 81

2 - X(CO2) H2O-CO2 MRK hybrid-EoS*

5 - X(CO2) H2O-CO2 CORK Holland & Powell 91, 98

8 - f(O2/CO2) C-buffered COH MRK hybrid-EoS*

10 - X(O) C-buffered COH MRK hybrid-EoS Connolly & Cesare 93*

12 - X(O)-f(S2) C-buffered COHS MRK hybrid-EoS Connolly & Cesare 93*

13 - X(H2) H2O-H2 MRK hybrid-EoS*

14 - X(CO2) H2O-CO2 Pitzer & Sterner 94; Holland & Powell mixing 03

15 - X(H2) H2O-H2 low T MRK hybrid-EoS*

16 - X(O) H-O MRK hybrid-EoS*

17 - X(O)-f(S2) H-O-S MRK hybrid-EoS*

19 - X(O)-X(S) C-buffered COHS MRK hybrid-EoS Connolly & Cesare 93*

20 - X(O)-X(C) COHS MRK hybrid-EoS Connolly & Cesare 93*

24 - f(O2/CO2)-N/C C-buffered COHN MRK hybrid-EoS*

25 - X(CO2)-X(NaCl) H2O-CO2-NaCl Aranovich et al 10

26 - X(O) O-Si MRK Connolly 16

27 - X(O)-X(C) C-O-H MRK hybrid-EoS*

*Hybrid EoS use the following pure species EoS, to change these associations modify the hybrid_EoS keywords in the perplex_option file:

    H2O  - PSEoS Pitzer & Sterner 1994

    CO2  - PSEoS Pitzer & Sterner 1994

    CH4  - HSMRK Kerrick & Jacobs 1981

<span style="color:red">5</span>


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)?

<span style="color:red">n</span>


Select x-axis variable:

    1 - P(bar)

    2 - T(K)

    3 - Y(CO2)

    4 - Composition X_C1* (user defined)

*Although only one component is specified for the Y(CO2)   phase, its equation of state permits use of its compositional variable:

*X_C1 can not be selected as the y-axis variable

<span style="color:red">4</span>


Select y-axis variable:

    1 - P(bar)

    2 - T(K)

    3 - Y(CO2)

<span style="color:red">2</span>


Enter minimum and maximum values, respectively, for: T(K)

<span style="color:red">573</span>

<span style="color:red">1273</span>

Specify sectioning value for: P(bar)

5000

Specify sectioning value for: Y(CO2)

The fluid is pure CO2.

1

For gridded minimization, grid resolution is determined by the number of levels (grid_levels) and the resolution at the lowest level in the X- and Y-directions (x_nodes and y_nodes) these parameters are currently set for the exploratory and autorefine cycles as follows:

stage      grid_levels xnodes ynodes   effective resolution

exploratory    1      40    40      40 x  40 nodes

auto-refine    4      40    40     313 x 313 nodes

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

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

Specify component amounts by mass (Y/N)?

N

The amounts you enter next need not be normalized; regardless of units, they define the molar amount of the system

The bulk composition of the system will be computed as:

  C = C0*(1 - X_C1) + C1*X_C1

where X_C1 varies between 0 and 1, and C0 and C1 are the compositions specified next.

To compute bulk compositions as:    C = C0 + C1*X_C1 change the computational option keyword closed_c_space.

Enter the molar amounts of the components:

 MgO   CaO

to define the composition C0

Composition C0 should be CaCO3, therefore it is defined as CaO=1, MgO=0

0

1

Enter the molar amounts of the components:

 MgO   CaO

to define the composition C1

Composition C1 should be MgCO3, therefore it is defined as CaO=0, MgO=1

1

0

Output a print file (Y/N)?

y

**warning ver051** cannot make hmjL     because of missing data or an invalid definition in the thermodynamic data file.

…

Exclude pure and/or endmember phases (Y/N)?

Y

Do you want to be prompted for phases (Y/N)?

n

Enter names, 1 per line, press <enter> to finish:

per

dol

See below the reason why the dol end-member is excluded from the calculation.

Include solution models (Y/N)?

Y

Enter the solution model file name [default = solution_model.dat]:

[enter]

…

Select models from the following list, enter 1 per line, press <enter> to finish
  Do(AE)   Cc(AE)   oCcM(HP)  Carb(M)   oCcM(EF)  dis(EF)
For details on these models see:www.perplex.ethz.ch/perplex_solution_model_glossary.html or read the commentary in the solution model file.

Do(AE)

Cc(AE)

Do(AE) and Cc(AE) are the solution models for dolomite and magnesite from Anovitz & Essene (1987), respectively. Cc(AE) also models Mg-calcite.
*"The Do(AE) model requires fictive do-structure endmembers that have a standard state G 20920 j > than the Cal-structure endmember, these are made here by a "DQF" correction."* **This "warning" (see solution_model.dat file) implies that the dol end-member must be excluded from the calculation**.

Enter calculation title:

Ex6_5kbar

## (2) Doing the calculation (VERTEX)

Run VERTEX to make the calculation:

C:\PERPLEX\Perplex686>vertex

Perple_X version 6.8.6, source updated Jan 24, 2019.
Copyright (C) 1986-2019 James A D Connolly <www.perplex.ethz/copyright.html>.

Enter the project name (the name assigned in BUILD) [default = my_project]:

ex6_5kbar

Reading problem definition from file: ex6_5kbar.dat
Reading thermodynamic data from file: hp62ver.dat
Reading solution models from file: solution_model.dat
Writing print output to file: ex6_5kbar.prn
Writing plot output to file: ex6_5kbar.plt
Writing bulk composition plot output to file: ex6_5kbar.blk

Reading Perple_X options from: perplex_option.dat
Writing auto refine summary to file: not requested
Writing pseudocompound glossary to file: ex6_5kbar_pseudocompound_glossary.txt
Writing Perple_X option summary to file: not requested

Perple_X version 6.8.6, source updated Jan 24, 2019.
Copyright (C) 1986-2019 James A D Connolly <www.perplex.ethz/copyright.html>.

Perple_X computational option settings for VERTEX:
  Keyword:          Value:    Permitted values [default]:
 Auto-refine options:
   auto_refine        auto      off manual [auto]
 Free energy minimization options:
  final_resolution:
    exploratory stage    0.1E-1   [1e-2], target value, see actual values be low
    auto-refine stage    0.1E-2   [1e-3], target value, see actual values be low
   resolution_factor    2        >= 2 [2]
   refinement_points    4        [aut] or 1->12; aut = automatic
   solvus_tolerance_II   aut      0->1 [0.2]
   global_reach_increment  0       >= 0 [0]
   reach_increment_switch  on      [on] off all
   zero_mode          0.1E-05  0->1 [1e-6]; < 0 => off
 2D grid options:
   x_nodes          40 / 40   [20/40], >0, <2048; effective x-resolution   60 / 313 nodes
   y_nodes          40 / 40   [20/40], >0, <2048; effective y-resolution   60 / 313 nodes
   grid_levels        1 / 4    [1/4], >0, <10
   linear_model        on      off [on]
 Composition options:
   closed_c_space       T       F [T]
 Solution subdivision options:
     initial_resolution:
    exploratory stage   0.0625    0->1 [1/16], 0 => off
    auto-refine stage   0.0208    0->1 [1/48 ], 0 => off
   stretch_factor       0.0020    >0 [2d-3]
   subdivision_override  off      [off] lin str
   hard_limits        off      [off] on
   refine_endmembers     F       [F] T
 Thermodynamic options:
   solvus_tolerance      aut      [aut] or 0->1; aut = automatic, 0 => p=c pseudocompounds, 1 => homogenize
   T_stop (K)          0.0     [0]
   T_melt (K)          873.0    [873]
   order_check         on      off [on]
   approx_alpha         T       [T] F
   Anderson-Gruneisen     F       [F] T
   speciation_factor      100.     >10 [100] speciation precision = final resolution/speciation_factor
   speciation_max_it     100     [100]
   hybrid_EoS_H2O        4       [4] 0-2, 4-7
   hybrid_EoS_CO2        4       [4] 0-4, 7
   hybrid_EoS_CH4        0       [0] 0-1, 7
   aq_bad_results       err      [err] 101, 102, 103, ignore
   aq_lagged_speciation  F       [F] T

```
aq_ion_H+   T   [T] F => use OH-
aq_oxide_components F   [F] T
aq_solvent_solvus   T   [T] F
aq_vapor_epsilon   1.0   [1.]
Input/Output options:
dependent_potentials off   off [on]
pause_on_error   T   [T] F
auto_exclude   T   [T] F
logarithmic_p   F   [F] T
bad_number   NaN   [NaN]
interim_results   aut   [auto] off manual
Information file output options:
option_list_files   F   [F] T; echo computational options
pseudocompound_file F   [F] T; echo static pseudocompound compositions
auto_refine_file   F   [F] T; echo auto-refine compositions
Worst case (Cartesian) compositional resolution (mol):
Exploratory stage: 0.521E-2
Auto-refine stage: 0.868E-3
Adapative minimization will be done with:
4 iterations in the exploratory stage
5 iterations in the autorefine stage
```
To change these options see: www.perplex.ethz.ch/perplex_options.html

…

**warning ver114** the following endmembers are missing for Do(AE)
 sid
    15 pseudocompounds generated for: Do(AE)

**warning ver114** the following endmembers are missing for Cc(AE)
 sid
    15 pseudocompounds generated for: Cc(AE)
Total number of pseudocompounds:     30

This is the total number of pseudocompounds considered by VERTEX; the number of pseudocompounds is controlled by some of the perplex_option keywords. **The highest is the number of pseudocompounds, the longest is the calculation (and the virtual memory consumed).**

**For pseudosection calculations (involving solid solutions), VERTEX divides the calculation in two stages.** The **EXPLORATORY STAGE** is used to roughly establish the stable solution compositions; in the **AUTO-REFINE STAGE**, VERTEX refines the previous calculation by:
1) Eliminating solutions that were not stable in the exploratory calculation.
2) Restricting compositional ranges of solutions to the ranges established in the exploratory calculation
3) Increasing resolution of compositions within these restricted ranges.

This is the beginning of EXPLORATORY STAGE
** Starting exploratory computational stage **
 2.5% done with low level grid.

5.0% done with low level grid.
7.5% done with low level grid.
10.0% done with low level grid.
12.5% done with low level grid.
15.0% done with low level grid.
17.5% done with low level grid.
20.0% done with low level grid.
22.5% done with low level grid.
25.0% done with low level grid.
27.5% done with low level grid.
30.0% done with low level grid.
32.5% done with low level grid.
35.0% done with low level grid.
37.5% done with low level grid.
40.0% done with low level grid.
42.5% done with low level grid.
45.0% done with low level grid.
47.5% done with low level grid.
50.0% done with low level grid.
52.5% done with low level grid.
55.0% done with low level grid.
57.5% done with low level grid.
60.0% done with low level grid.
62.5% done with low level grid.
65.0% done with low level grid.
67.5% done with low level grid.
70.0% done with low level grid.
72.5% done with low level grid.
75.0% done with low level grid.
77.5% done with low level grid.
80.0% done with low level grid.
82.5% done with low level grid.
85.0% done with low level grid.
87.5% done with low level grid.
90.0% done with low level grid.
92.5% done with low level grid.
95.0% done with low level grid.
97.5% done with low level grid.
100.0% done with low level grid.

Endmember fractions for model: Do(AE)
    Endmember    Minimum       Maximum
    cc        0.48438       0.56250
Endmember fractions for model: Cc(AE)
    Endmember    Minimum       Maximum
    mag        0.0000        1.0000
Reading data for auto-refinement from file: ex6_5kbar.arf

    6 pseudocompounds generated for: Do(AE)
    47 pseudocompounds generated for: Cc(AE)
Total number of pseudocompounds:     53

This is the beginning of the AUTO-REFINE STAGE
** Starting auto_refine computational stage **
 0.3% done with low level grid.
 2.9% done with low level grid.
 5.4% done with low level grid.
 8.0% done with low level grid.
10.5% done with low level grid.
13.1% done with low level grid.
15.7% done with low level grid.
18.2% done with low level grid.
20.8% done with low level grid.
23.3% done with low level grid.
25.9% done with low level grid.
28.4% done with low level grid.
31.0% done with low level grid.
33.5% done with low level grid.
36.1% done with low level grid.
38.7% done with low level grid.
41.2% done with low level grid.
43.8% done with low level grid.
46.3% done with low level grid.
48.9% done with low level grid.
51.4% done with low level grid.
54.0% done with low level grid.
56.5% done with low level grid.
59.1% done with low level grid.
61.7% done with low level grid.
64.2% done with low level grid.
66.8% done with low level grid.
69.3% done with low level grid.
71.9% done with low level grid.
74.4% done with low level grid.
77.0% done with low level grid.
79.6% done with low level grid.
82.1% done with low level grid.
84.7% done with low level grid.
87.2% done with low level grid.
89.8% done with low level grid.
92.3% done with low level grid.
94.9% done with low level grid.
97.4% done with low level grid.
100.0% done with low level grid.

Beginning grid refinement stage.
   167 grid cells to be refined at grid level 2
      refinement at level 2 involved    353 minimizations
  1953 minimizations required of the theoretical limit of    6241
   321 grid cells to be refined at grid level 3
      ...working (   148 minimizations done)
      refinement at level 3 involved    632 minimizations

2585 minimizations required of the theoretical limit of   24649
 630 grid cells to be refined at grid level 4
    ...working (    17 minimizations done)
    ...working (   519 minimizations done)
    ...working (  1020 minimizations done)
    refinement at level 4 involved   1229 minimizations
 3814 minimizations required of the theoretical limit of  98596


Endmember fractions for model: Do(AE)
   Endmember    Minimum       Maximum
    cc      0.48264      0.56424
Endmember fractions for model: Cc(AE)
   Endmember    Minimum       Maximum
    mag       0.0000       1.0000


Before plotting the calculated diagram, have a look to the new pseudocompound_file.txt generated by VERTEX. It contains the list of the pseudocompounds with their composition.


## (3) Plotting the calculated phase diagram (PSSECT)

Run PSSECT to plot the calculated pseudosection:

C:\PERPLEX\Perplex685(090118)>pssect

Perple_X version 6.8.5, source updated Dec 22, 2018.
Copyright (C) 1986-2018 James A D Connolly <www.perplex.ethz/copyright.html>.

Enter the project name (the name assigned in BUILD) [default = my_project]:
ex6_5kbar

Reading Perple_X options from: perplex_option.dat
Perple_X plot options are currently set as:
   Keyword:          Value:    Permitted values [default]:
   axis_label_scale     1.20      [1.2] (rel)
   bounding_box :
                0    [0] x-min (pts)
                0    [0] y-min (pts)
              800     [800] x-length (pts)
              800     [800] y-length (pts)
   field_fill        T       [T] F
   field_label        T       [T] F
   field_label_scale     0.75      [0.72] (rel)
   font           Helvetica
   grid           F       [F] T
   half_ticks        T       [T] F
   line_width        1.00      0-99 [1.] (pts)
   picture_transformation :
              0.180    [0.18] x-scale (rel)
              0.180    [0.18] y-scale (rel)
               130.    [0.18] x-translation (pts)

          220.    [0.18] y-translation (pts)
          0.00    [0.0]  rotation (deg)
  plot_aspect_ratio    1.000    [1.0] x_axis_length/y_axis_length
  replicate_label    0.250    0->1 [0.025]
  splines        T      [T] F
  tenth_ticks      F      [F] T
  text_scale      1.000    [1.] (rel)
To change these options edit or create the plot option file
See: www.perplex.ethz.ch/perplex_plot_options.html

PostScript will be written to file: ex6_5kbar.ps

Modify the default plot (y/n)?
n
There are  2 fields for: Cc

Because the Cc(AE) solution model treats simultaneously both the Mg-calcite and magnesite solid solutions, they are indicated with the same name on the diagram. Be careful to assign the correct name to each phase.



In the resulting diagram there are two different types of fields: white fields contain two phases (these are the miscibility gaps), whereas grey fields contain one phase. White fields are di-variant, and grey-field are tri-variant.

The red ellipse highlights a "bug", that can be eliminated by increasing the resolution of the x-y grid used by VERTEX during the gridded minimization calculation.

# (4) Increasing the resolution of the x-y grid

For gridded minimization, VERTEX uses a multilevel grid refinement strategy in which phase relations are mapped on an initial grid of resolution x_nodes * y_nodes. This grid is refined a number of times equal to (grid_levels − 1) by bisection (Connolly 2005). The x_nodes, y_nodes, grid_levels parameters are set by keywords of the same name in the perplex_option file. Each keyword takes two integer values. The first value is used for the exploratory stage of gridded minimization calculations, while the second value is used for the auto-refine stage.

There is no simple rule for the best choices for x_nodes or y_nodes as they depend on the scale of the diagram and the heterogeneity of its phase fields, the default values are 40 and 40 for exploratory and auto-refinement stages of a calculation. The default values of grid_levels are 1 and 4 for exploratory and auto-refinement stages.

Increase the resolution of the grid, by increasing the number of x-y nodes for the auto-refinement stage of calculation from 40 to 60 (open the perplex_option.dat file and modify the default value of the x_nodes and y_nodes parameters).

x_nodes    40 60 | [40 40] exploratory and auto-refine (grid parameters keyword group), lowest-level
           x grid resolution
y_nodes    40 60 | [40 40] exploratory and auto-refine (grid parameters keyword group), lowest-level
           y grid resolution

Run VERTEX and PSSECT again and see the result. The problem has been solved.

## (5) Exploring the influence of pressure on the Cal-Dol and Dol-Mag *solvi*

The influence of pressure on the Cal-Dol and Dol-Mag *solvi* can be investigated by calculating the same phase diagram at different pressures (5 to 30 kbar, every 5 kbar). You can **edit the input file**, by specifying a different pressure (**remember to rename the file**). Pressure is reported at the end of the input file:

```
5000.00    1273.00    1.00000    0.00000    0.00000    max p, t, xco2, u1, u2
5000.00    573.000    1.00000    0.00000    0.00000    min p, t, xco2, u1, u2
0.00000    0.00000    0.00000    0.00000    0.00000    unused place holder post 06
```

Run again VERTEX and PSESECT for calculation at 10, 15, 20, 25 and 30 kbar, respectively.

What happens at the T (and P) conditions indicated by the blue, red and orange arrows?

How many phases are stable at those P-T conditions?

Ex. 7

Ex. 7 – P-T projection for the CaCO₃-MgCO₃ system using solid solutions

This exercise explains how to calculate a P-T projection for the CaCO₃-MgCO₃ system, using solid solutions (rather than end members only).

Combined with Ex. 6, this exercise provides the opportunity for understanding the relationships between isobaric T-X sections and P-T projections.

(1) Definition of the problem (BUILD)

C:\PERPLEX\Perplex686>build

Perple_X version 6.8.6, source updated Jan 24, 2019.
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NO is the default (blank) answer to all Y/N prompts

Enter a name for this project (the name will be used as the root for all output file names) [default = my_project]:
ex7

The problem definition file will be named: ex7.dat

Enter thermodynamic data file name [default = hp02ver.dat]:
hp62ver.dat

Enter the computational option file name [default = perplex_option.dat]:
See: www.perplex.ethz.ch/perplex_options.html

Reading Perple_X options from: perplex_option.dat

The current data base components are:
 Na2O MgO Al2O3 SiO2 K2O CaO TiO2 MnO FeO NiO ZrO2 Cl2 O2   H2O CO2 CuO Cr2O3 S2 F2
Transform them (Y/N)?
n

Specify computational mode:
   1 - Convex-Hull minimization
   2 - Constrained minimization on a 2d grid [default]
   3 - Constrained minimization on a 1d grid
   4 - Output pseudocompound data
   5 - 1-d Phase fractionation calculations
   6 - 0-d Infiltration-reactionation-fractionation
   7 - 2-d Phase fractionation (FRAC2D and TITRATE reactive transport models)
Use Convex-Hull minimization for Schreinemakers projections or phase diagrams with > 2 independent variables. Use constrained minimization for phase diagram or phase diagram sections with < 3 independent variables.

1

Calculations with a saturated fluid (Y/N)?
y

Select the independent saturated fluid components:
 H2O CO2
Enter names, 1 per line, press <enter> 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.
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   H2O CuO Cr2O3 S2   F2
Enter names, 1 per line, press <enter> to finish:
MgO
CaO

Because the thermodynamic data file identifies: CO2 as special components, you will be prompted next for the EoS to be used for the corresponding composants and mixtures thereof. To override this behavior, e.g., to use a generic hybrid fluid EoS, delete the special_component section from the thermodynamic data file header.

Select fluid equation of state:
  0 - X(CO2) H2O-CO2 Modified Redlich-Kwong (MRK) DeSantis et al 74
  1 - X(CO2) H2O-CO2 HSMRK Kerrick & Jacobs 81
  2 - X(CO2) H2O-CO2 MRK hybrid-EoS*
  5 - X(CO2) H2O-CO2 CORK Holland & Powell 91, 98
  8 - f(O2/CO2) C-buffered COH MRK hybrid-EoS*
 10 - X(O) C-buffered COH MRK hybrid-EoS Connolly & Cesare 93*
 12 - X(O)-f(S2) C-buffered COHS MRK hybrid-EoS Connolly & Cesare 93*
 13 - X(H2) H2O-H2 MRK hybrid-EoS*
 14 - X(CO2) H2O-CO2 Pitzer & Sterner 94; Holland & Powell mixing 03
 15 - X(H2) H2O-H2 low T MRK hybrid-EoS*
 16 - X(O) H-O MRK hybrid-EoS*
 17 - X(O)-f(S2) H-O-S MRK hybrid-EoS*
 19 - X(O)-X(S) C-buffered COHS MRK hybrid-EoS Connolly & Cesare 93*
 20 - X(O)-X(C) COHS MRK hybrid-EoS Connolly & Cesare 93*
 24 - f(O2/CO2)-N/C C-buffered COHN MRK hybrid-EoS*
 25 - X(CO2)-X(NaCl) H2O-CO2-NaCl Aranovich et al 10
 26 - X(O) O-Si MRK Connolly 16
 27 - X(O)-X(C) C-O-H MRK hybrid-EoS*

*Hybrid EoS use the following pure species EoS, to change these associations modify the hybrid_EoS keywords in the perplex_option file:

    H2O - PSEoS Pitzer & Sterner 1994

    CO2 - PSEoS Pitzer & Sterner 1994

    CH4 - HSMRK Kerrick & Jacobs 1981

5

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

2

Select x-axis variable:

    1 - P(bar)

    2 - T(K)

    3 - Y(CO2)

*Although only one component is specified for the Y(CO2)   phase, its equation of state permits use of its compositional variable:

2

Enter minimum and maximum values, respectively, for: T(K)

573

1273

Same T range as in Ex. 6

Select y-axis variable:

    2 - P(bar)

    3 - Y(CO2)

2

Enter minimum and maximum values, respectively, for: P(bar)

5000

30000

Same P range as in Ex. 6

Specify sectioning value for: Y(CO2)

1

Output a print file (Y/N)?

y

…

Exclude pure and/or endmember phases (Y/N)?

y

Do you want to be prompted for phases (Y/N)?

n
Enter names, 1 per line, press <enter> to finish:
per
dol
Same as in Ex. 6

Include solution models (Y/N)?
y
Enter the solution model file name [default = solution_model.dat]:
[enter]
…
Select models from the following list, enter 1 per line, press <enter> to finish
  Do(AE)   Cc(AE)   oCcM(HP) Carb(M)   oCcM(EF) dis(EF)
For details on these models see:www.perplex.ethz.ch/perplex_solution_model_glossary.html or read the commentary in the solution model file.
Do(AE)
Cc(AE)
Same as in Ex. 6

Enter calculation title:
ex7

(2) Doing the calculation (CONVEX)

Run CONVEX to make the calculation:

C:\PERPLEX\Perplex686>convex

Perple_X version 6.8.6, source updated Jan 24, 2019.
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Enter the project name (the name assigned in BUILD) [default = my_project]:
Ex7

Reading problem definition from file: ex7.dat
Reading thermodynamic data from file: hp62ver.dat
Reading solution models from file: solution_model.dat
Writing print output to file: ex7.prn
Writing plot output to file: ex7.plt
Reading Perple_X options from: perplex_option.dat
Writing complete reaction list to file: not requested
Writing auto refine summary to file: not requested
Writing pseudocompound glossary to file: ex7_pseudocompound_glossary.txt
Writing Perple_X option summary to file: not requested

Perple_X version 6.8.6, source updated Jan 24, 2019.
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Perple_X computational option settings for CONVEX:

```
   Keyword:        Value:    Permitted values [default]:
 Auto-refine options:
  auto_refine        aut      off manual [auto]
 Schreinemakers and Mixed-variable diagram options:
  variance          1 /99    [1/99], >0, maximum true variance
  increment         0.100/0.025  [0.1/0.025], default search/trace variable  increment
  efficiency        3       [3] >0 < 6
  reaction_format   min     [min] full stoichiometry S+V everything
  reaction_list     off     [off] on
  console_messages  on      [on] off
  short_print_file  on      [on] off
 Solution subdivision options:
  initial_resolution:
    exploratory stage   0.0625    0->1 [1/16], 0 => off
    auto-refine stage   0.0208    0->1 [1/48 ], 0 => off
  stretch_factor     0.0020    >0 [2d-3]
  subdivision_override   off     [off] lin str
  hard_limits        off     [off] on
  refine_endmembers    F      [F] T
  pc_perturbation     0.0050    [5d-3]
 Thermodynamic options:
  solvus_tolerance    aut     [aut] or 0->1; aut = automatic, 0 => p=c pseudocompounds, 1 => homogenize
  T_stop (K)        0.0    [0]
  T_melt (K)        873.0    [873]
  order_check       on      off [on]
  approx_alpha      T       [T] F
  Anderson-Gruneisen   F      [F] T
  speciation_factor     100.    >10 [100] speciation precision = final resolution/speciation_factor
  speciation_max_it    100    [100]
  hybrid_EoS_H2O       4     [4] 0-2, 4-7
  hybrid_EoS_CO2       4     [4] 0-4, 7
  hybrid_EoS_CH4       0     [0] 0-1, 7
  aq_bad_results      err     [err] 101, 102, 103, ignore
  aq_lagged_speciation  F      [F] T
  aq_ion_H+         T      [T] F => use OH-
  aq_oxide_components   F      [F] T
  aq_solvent_solvus    T      [T] F
  aq_vapor_epsilon    1.0     [1.]
 Input/Output options:
  dependent_potentials   off     off [on]
  pause_on_error      T       [T] F
  auto_exclude       T       [T] F
 Worst case (Cartesian) compositional resolution (mol):
  Exploratory stage:   0.521E-2
  Auto-refine stage:   0.868E-3
 Adapative minimization will be done with:
   4 iterations in the exploratory stage
   5 iterations in the autorefine stage
To change these options see: www.perplex.ethz.ch/perplex_options.html

…
```

warning ver114 the following endmembers are missing for Do(AE)
  sid
     15 pseudocompounds generated for: Do(AE)
warning ver114 the following endmembers are missing for Cc(AE)
  sid
     15 pseudocompounds generated for: Cc(AE)
Total number of pseudocompounds: 30

** Starting exploratory computational stage **
cycle   1   1   1
 cycle   2   2   2
Initial number of divariant assemblages to be tested is: 2
Testing divariant assemblage   1,   1 assemblages remaining to be tested.
Testing divariant assemblage   2,   2 assemblages remaining to be tested.
Testing divariant assemblage   3,   3 assemblages remaining to be tested.
Testing divariant assemblage   4,   4 assemblages remaining to be tested.
Testing divariant assemblage   5,   4 assemblages remaining to be tested.
warning ver066 Metastable assemblage into FLIPIT:
   mag_6.2 cc
v = 7517.30   573.000   1.00000   0.00000   0.00000
Testing divariant assemblage   6,   4 assemblages remaining to be tested.
Testing divariant assemblage   7,   5 assemblages remaining to be tested.
Testing divariant assemblage   8,   5 assemblages remaining to be tested.
Testing divariant assemblage   9,   5 assemblages remaining to be tested.
warning ver066 Metastable assemblage into FLIPIT:
   mag   arag
v = 30000.0   895.993   1.00000   0.00000   0.00000
Testing divariant assemblage   10,   6 assemblages remaining to be tested.
warning ver066 Metastable assemblage into FLIPIT:
   mag_6.2 arag
v = 27500.0   1273.00   1.00000   0.00000   0.00000
Testing divariant assemblage   11,   5 assemblages remaining to be tested.
Testing divariant assemblage   12,   4 assemblages remaining to be tested.
Testing divariant assemblage   13,   5 assemblages remaining to be tested.
Testing divariant assemblage   14,   5 assemblages remaining to be tested.
Testing divariant assemblage   15,   4 assemblages remaining to be tested.
Testing divariant assemblage   16,   4 assemblages remaining to be tested.
Testing divariant assemblage   17,   3 assemblages remaining to be tested.
Testing divariant assemblage   18,   3 assemblages remaining to be tested.
Testing divariant assemblage   19,   4 assemblages remaining to be tested.
Testing divariant assemblage   20,   4 assemblages remaining to be tested.
Testing divariant assemblage   21,   3 assemblages remaining to be tested.
Testing divariant assemblage   22,   3 assemblages remaining to be tested.
Testing divariant assemblage   23,   3 assemblages remaining to be tested.
Testing divariant assemblage   24,   2 assemblages remaining to be tested.
Testing divariant assemblage   25,   2 assemblages remaining to be tested.
warning ver066 Metastable assemblage into FLIPIT:
   arag   mag_18.8
v = 30000.0   1133.00   1.00000   0.00000   0.00000
Testing divariant assemblage   26,   1 assemblages remaining to be tested.
Testing divariant assemblage   27,   0 assemblages remaining to be tested.

Endmember fractions for model: Do(AE)

   Endmember   Minimum   Maximum

    cc   0.50000   0.56250

Endmember fractions for model: Cc(AE)

   Endmember   Minimum   Maximum

    mag   0.62500E-01   0.93750

Reading data for auto-refinement from file: ex7.arf

   10 pseudocompounds generated for: Do(AE)

   47 pseudocompounds generated for: Cc(AE)

Total number of pseudocompounds: 57

** Starting auto_refine computational stage **

cycle   1   1   1

 cycle   2   2   2

 cycle   3   3   3

 cycle   4   4   4

Initial number of divariant assemblages to be tested is: 4

Testing divariant assemblage   1,   3 assemblages remaining to be tested.

finished with equilibrium (1) Cc(AE)(mag) Do(AE)(cc_47.9) = Cc(AE)(mag_97.9)

finished with equilibrium (2) Cc(AE)(mag) arag = Do(AE)(cc_47.9)

finished with equilibrium (3) Cc(AE)(mag) arag = Cc(AE)(mag_97.9)

finished with equilibrium (4) Cc(AE)(mag_97.9) arag = Do(AE)(cc_47.9)

finished with equilibrium (5) Do(AE)(cc_47.9) = Cc(AE)(mag_97.9) Do(AE)(cc_50.0)

finished with equilibrium (6) Do(AE)(cc_47.9) arag = Do(AE)(cc_50.0)

finished with equilibrium (7) Cc(AE)(mag_97.9) arag = Do(AE)(cc_50.0)

finished with equilibrium (8) Cc(AE)(mag_97.9) arag = Cc(AE)(mag_95.8)

finished with equilibrium (9) Cc(AE)(mag_97.9) Do(AE)(cc_50.0) = Cc(AE)(mag_95.8)

finished with equilibrium (10) arag Cc(AE)(mag_95.8) = Do(AE)(cc_50.0)

Testing divariant assemblage   2,   4 assemblages remaining to be tested.

Testing divariant assemblage   3,   4 assemblages remaining to be tested.

finished with equilibrium (11) Do(AE)(cc_50.0) Cc(AE)(mag_2.1) = Cc(AE)(mag_4.2)

finished with equilibrium (12) Do(AE)(cc_50.0) arag = Cc(AE)(mag_2.1)

finished with equilibrium (13) Do(AE)(cc_50.0) arag = Cc(AE)(mag_4.2)

finished with equilibrium (14) Cc(AE)(mag_4.2) arag = Cc(AE)(mag_2.1)

finished with equilibrium (15) Do(AE)(cc_50.0) Cc(AE)(mag_4.2) = Do(AE)(cc_52.1)

finished with equilibrium (16) Do(AE)(cc_50.0) arag = Do(AE)(cc_52.1)

finished with equilibrium (17) arag Do(AE)(cc_52.1) = Cc(AE)(mag_4.2)

finished with equilibrium (18) arag Cc(AE)(mag_6.2) = Cc(AE)(mag_4.2)

finished with equilibrium (19) Cc(AE)(mag_4.2) Do(AE)(cc_52.1) = Cc(AE)(mag_6.2)

finished with equilibrium (20) arag Do(AE)(cc_52.1) = Cc(AE)(mag_6.2)

finished with equilibrium (21) arag Do(AE)(cc_52.1) = Cc(AE)(mag_8.3)

finished with equilibrium (22) arag Cc(AE)(mag_8.3) = Cc(AE)(mag_6.2)

finished with equilibrium (23) Do(AE)(cc_52.1) Cc(AE)(mag_6.2) = Cc(AE)(mag_8.3)

finished with equilibrium (24) arag Do(AE)(cc_52.1) = Do(AE)(cc_54.2)

finished with equilibrium (25) arag Do(AE)(cc_54.2) = Cc(AE)(mag_8.3)

finished with equilibrium (26) Do(AE)(cc_52.1) Cc(AE)(mag_8.3) = Do(AE)(cc_54.2)

finished with equilibrium (27) arag Cc(AE)(mag_10.4) = Cc(AE)(mag_8.3)

finished with equilibrium (28) arag Do(AE)(cc_54.2) = Cc(AE)(mag_10.4)

finished with equilibrium (29) Cc(AE)(mag_8.3) Do(AE)(cc_54.2) = Cc(AE)(mag_10.4)

finished with equilibrium (30) arag Do(AE)(cc_54.2) = Cc(AE)(mag_12.5)
finished with equilibrium (31) arag Cc(AE)(mag_12.5) = Cc(AE)(mag_10.4)
finished with equilibrium (32) Do(AE)(cc_54.2) Cc(AE)(mag_10.4) = Cc(AE)(mag_12.5)
finished with equilibrium (33) arag Do(AE)(cc_54.2) = Cc(AE)(mag_14.6)
finished with equilibrium (34) arag Cc(AE)(mag_14.6) = Cc(AE)(mag_12.5)
finished with equilibrium (35) Do(AE)(cc_54.2) Cc(AE)(mag_12.5) = Cc(AE)(mag_14.6)
finished with equilibrium (36) arag Do(AE)(cc_54.2) = Do(AE)(cc_56.2)
finished with equilibrium (37) arag Do(AE)(cc_56.2) = Cc(AE)(mag_14.6)
finished with equilibrium (38) Do(AE)(cc_54.2) Cc(AE)(mag_14.6) = Do(AE)(cc_56.2)
finished with equilibrium (39) arag Cc(AE)(mag_16.7) = Cc(AE)(mag_14.6)
finished with equilibrium (40) arag Do(AE)(cc_56.2) = Cc(AE)(mag_16.7)
finished with equilibrium (41) Cc(AE)(mag_14.6) Do(AE)(cc_56.2) = Cc(AE)(mag_16.7)
Testing divariant assemblage   4,   5 assemblages remaining to be tested.
finished with equilibrium (42) arag = Cc(AE)(cc)
Testing divariant assemblage   5,   5 assemblages remaining to be tested.
Testing divariant assemblage   6,   4 assemblages remaining to be tested.
Testing divariant assemblage   7,   4 assemblages remaining to be tested.
Testing divariant assemblage   8,   5 assemblages remaining to be tested.
Testing divariant assemblage   9,   5 assemblages remaining to be tested.
Testing divariant assemblage   10,   6 assemblages remaining to be tested.
Testing divariant assemblage   11,   5 assemblages remaining to be tested.
Testing divariant assemblage   12,   5 assemblages remaining to be tested.
Testing divariant assemblage   13,   5 assemblages remaining to be tested.
finished with equilibrium (43) Cc(AE)(mag_95.8) Do(AE)(cc_50.0) = Cc(AE)(mag_93.8)
Testing divariant assemblage   14,   7 assemblages remaining to be tested.
Testing divariant assemblage   15,   7 assemblages remaining to be tested.
finished with equilibrium (44) Do(AE)(cc_50.0) = Do(AE)(cc_52.1) Cc(AE)(mag_91.7)
Testing divariant assemblage   16,   8 assemblages remaining to be tested.
Testing divariant assemblage   17,   9 assemblages remaining to be tested.
Testing divariant assemblage   18,   9 assemblages remaining to be tested.
Testing divariant assemblage   19,   8 assemblages remaining to be tested.
finished with equilibrium (45) Cc(AE)(mag_93.8) Do(AE)(cc_50.0) = Cc(AE)(mag_91.7)
Testing divariant assemblage   20,   10 assemblages remaining to be tested.
Testing divariant assemblage   21,   9 assemblages remaining to be tested.
Testing divariant assemblage   22,   8 assemblages remaining to be tested.
Testing divariant assemblage   23,   8 assemblages remaining to be tested.
finished with equilibrium (46) Do(AE)(cc_52.1) Cc(AE)(mag_91.7) = Cc(AE)(mag_89.6)
Testing divariant assemblage   24,   10 assemblages remaining to be tested.
Testing divariant assemblage   25,   11 assemblages remaining to be tested.
Testing divariant assemblage   26,   10 assemblages remaining to be tested.
Testing divariant assemblage   27,   11 assemblages remaining to be tested.
Testing divariant assemblage   28,   10 assemblages remaining to be tested.
Testing divariant assemblage   29,   10 assemblages remaining to be tested.
Testing divariant assemblage   30,   9 assemblages remaining to be tested.
Testing divariant assemblage   31,   9 assemblages remaining to be tested.
Testing divariant assemblage   32,   9 assemblages remaining to be tested.
Testing divariant assemblage   33,   9 assemblages remaining to be tested.
finished with equilibrium (47) Cc(AE)(mag_89.6) Do(AE)(cc_52.1) = Cc(AE)(mag_87.5)
Testing divariant assemblage   34,   10 assemblages remaining to be tested.
Testing divariant assemblage   35,   9 assemblages remaining to be tested.
Testing divariant assemblage   36,   9 assemblages remaining to be tested.

Testing divariant assemblage   37,   8 assemblages remaining to be tested.
Testing divariant assemblage   38,   9 assemblages remaining to be tested.
Testing divariant assemblage   39,   9 assemblages remaining to be tested.
Testing divariant assemblage   40,   9 assemblages remaining to be tested.
Testing divariant assemblage   41,   8 assemblages remaining to be tested.
Testing divariant assemblage   42,   8 assemblages remaining to be tested.
Testing divariant assemblage   43,   9 assemblages remaining to be tested.
Testing divariant assemblage   44,   9 assemblages remaining to be tested.
Testing divariant assemblage   45,   8 assemblages remaining to be tested.
Testing divariant assemblage   46,   7 assemblages remaining to be tested.
Testing divariant assemblage   47,   7 assemblages remaining to be tested.
Testing divariant assemblage   48,   8 assemblages remaining to be tested.
Testing divariant assemblage   49,   7 assemblages remaining to be tested.
Testing divariant assemblage   50,   7 assemblages remaining to be tested.
Testing divariant assemblage   51,   7 assemblages remaining to be tested.
Testing divariant assemblage   52,   6 assemblages remaining to be tested.
Testing divariant assemblage   53,   6 assemblages remaining to be tested.
Testing divariant assemblage   54,   6 assemblages remaining to be tested.
Testing divariant assemblage   55,   5 assemblages remaining to be tested.
Testing divariant assemblage   56,   5 assemblages remaining to be tested.
Testing divariant assemblage   57,   6 assemblages remaining to be tested.
Testing divariant assemblage   58,   6 assemblages remaining to be tested.
Testing divariant assemblage   59,   6 assemblages remaining to be tested.
Testing divariant assemblage   60,   6 assemblages remaining to be tested.
Testing divariant assemblage   61,   5 assemblages remaining to be tested.
Testing divariant assemblage   62,   4 assemblages remaining to be tested.
Testing divariant assemblage   63,   5 assemblages remaining to be tested.
Testing divariant assemblage   64,   5 assemblages remaining to be tested.
Testing divariant assemblage   65,   5 assemblages remaining to be tested.
Testing divariant assemblage   66,   5 assemblages remaining to be tested.
Testing divariant assemblage   67,   5 assemblages remaining to be tested.
Testing divariant assemblage   68,   6 assemblages remaining to be tested.
Testing divariant assemblage   69,   6 assemblages remaining to be tested.
Testing divariant assemblage   70,   5 assemblages remaining to be tested.
Testing divariant assemblage   71,   4 assemblages remaining to be tested.
Testing divariant assemblage   72,   4 assemblages remaining to be tested.
Testing divariant assemblage   73,   4 assemblages remaining to be tested.
Testing divariant assemblage   74,   3 assemblages remaining to be tested.
Testing divariant assemblage   75,   4 assemblages remaining to be tested.
Testing divariant assemblage   76,   3 assemblages remaining to be tested.
Testing divariant assemblage   77,   2 assemblages remaining to be tested.
Testing divariant assemblage   78,   2 assemblages remaining to be tested.
Testing divariant assemblage   79,   2 assemblages remaining to be tested.
finished with equilibrium (48) Cc(AE)(mag_16.7) Do(AE)(cc_56.2) = Cc(AE)(mag_18.8)
Testing divariant assemblage   80,   4 assemblages remaining to be tested.
Testing divariant assemblage   81,   3 assemblages remaining to be tested.
warning ver066 Metastable assemblage into FLIPIT:
    mag_16.7 arag
v = 30000.0   1150.50   1.00000   0.00000   0.00000
Testing divariant assemblage   82,   2 assemblages remaining to be tested.
finished with equilibrium (49) Cc(AE)(mag_18.8) Do(AE)(cc_56.2) = Cc(AE)(mag_20.8)

Testing divariant assemblage   83,   4 assemblages remaining to be tested.
Testing divariant assemblage   84,   3 assemblages remaining to be tested.
Testing divariant assemblage   85,   3 assemblages remaining to be tested.
Testing divariant assemblage   86,   3 assemblages remaining to be tested.
Testing divariant assemblage   87,   2 assemblages remaining to be tested.
Testing divariant assemblage   88,   1 assemblages remaining to be tested.
Testing divariant assemblage   89,   0 assemblages remaining to be tested.

Endmember fractions for model: Do(AE)
   Endmember   Minimum   Maximum
     cc   0.47917   0.56250
Endmember fractions for model: Cc(AE)
   Endmember   Minimum   Maximum
     mag   0.20833E-01   0.97917

(3) Plotting the calculated phase diagram (PSVDRAW)

Run PSWDRAW to plot the calculated pseudosection:

C:\PERPLEX\Perplex686>psvdraw

Perple_X version 6.8.6, source updated Jan 24, 2019.
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Enter the project or plot file name [i.e., without the .plt suffix]:
ex7

Perple_X plot options are currently set as:
   Keyword: Value: Permitted values [default]:
   axis_label_scale   1.20   [1.2] (rel)
   bounding_box :
                  0   [0] x-min (pts)
                  0   [0] y-min (pts)
                800   [800] x-length (pts)
                800   [800] y-length (pts)
   field_fill   T   [T] F
   field_label   T   [T] F
   field_label_scale   0.75   [0.72] (rel)
   font   Helvetica
   grid   F   [F] T
   half_ticks   T   [T] F
   line_width   1.00   0-99 [1.] (pts)
   picture_transformation :
              0.180   [0.18] x-scale (rel)
              0.180   [0.18] y-scale (rel)
               130.   [0.18] x-translation (pts)
               220.   [0.18] y-translation (pts)
              0.00   [0.0] rotation (deg)
   plot_aspect_ratio   1.000   [1.0] x_axis_length/y_axis_length
   replicate_label   0.250   0->1 [0.025]
   splines   T   [T] F

```
     tenth_ticks      F      [F] T
     text_scale       1.000   [1.] (rel)
```
To change these options edit or create the plot option fileSee: www.perplex.ethz.ch/perplex_plot_options.html
PostScript will be written to file: ex7.ps

Modify the default plot (y/n)?
Y
CONVEX has calculated both true univariant equilibria (i.e. variance = 1) and **pseudo-univariant equilibria (i.e. equilibria among pseudocompounds, involving two pseudocompounds of the same phase on both sides of the reaction; variance =2**). Pseudo-univariant equilibria are not true univariant reactions, and it is convenient not to plot them, otherwise the resulting diagram would be full of curves.

Modify drafting options (y/n)?
  answer yes to modify:
   - x-y plotting limits
   - axes numbering
n

Restrict phase fields by variance (y/n)?
  answer yes to:
   - suppress pseudounivariant curves and/or pseudoinvariant points of a specified true variance.
y
This is a key prompt. We are interested to "true" univariant reactions (i.e. true variance = 1), not to pseudo-univariant curves (i.e. di-variant equilibria involving two pseudocompounds of the same phase on both sides of the reaction). Therefore we must suppress all the curves that have a variance ≥2 (i.e. we must show all fields with true variance <2, see below).

Select true variance restriction to be applied to pseudo-invariant/univariant equilibria:
  1 - show all fields with true variance < than a specified value [default]
  2 - show all fields with a specified true variance
1
We are interested to "true" univariant reactions (i.e. true variance = 1), therefore we must show all fields with true variance <2.

Enter the true variance to be used for this restriction [1-99, default = 2]:
2

Suppress pseudoinvariant points (y/n)?
N
Pseudoinvariant points are useful for visualizing how a phase changes its composition along a true univariant curve (see below).
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
n

Modify default equilibrium labeling (y/n)?
  answer yes to:
   - modify/suppress [pseudo-] univariant curve labels
   - suppress [pseudo-] invariant point labels
y

Suppress curve labels (y/n)?
n

Change default labeling of curve segments (y/n)?
y

Suppress labels of pseudounivariant curves (y/n)?
y

Enter minimum fraction of the axes length that a
curve must be to receive a text label (0-1):
1 means that a text label will be assigned to those curves that are longer than the axes length.
1

Enter minimum fraction of the axes length that a
curve must be to receive a numeric label (0-1.000):
0 means that a numeric label will be assigned to all those curves that are shorter than the axes length.
0

Suppress point labels (y/n)?
N

The resulting diagram shows three univariant equilibria. Two of them are divided in several parts (each one with a numeric label) by pseudo-invariant points (small points, with number in brackets). The third univariant equilibrium is the polymorphic transformation of calcite to aragonite.
To understand the meaning of each part of the univariant equilibria, open the ex7.prn file. At the end of this file, the (pseudo-) univariant equilibria are summarized.

Mag + Arag = Dol
(2) Cc(AE)(mag) arag = Do(AE)(cc_47.9)
(4) Cc(AE)(mag_97.9) arag = Do(AE)(cc_47.9)
(7) Cc(AE)(mag_97.9) arag = Do(AE)(cc_50.0)
(10) arag Cc(AE)(mag_95.8) = Do(AE)(cc_50.0)

Arag + Dol = Mg-Cal
(12) Do(AE)(cc_50.0) arag = Cc(AE)(mag_2.1)
(13)Do(AE)(cc_50.0) arag = Cc(AE)(mag_4.2)
(17) arag Do(AE)(cc_52.1) = Cc(AE)(mag_4.2)
(20) arag Do(AE)(cc_52.1) = Cc(AE)(mag_6.2)
(21) arag Do(AE)(cc_52.1) = Cc(AE)(mag_8.3)
(25) arag Do(AE)(cc_54.2) = Cc(AE)(mag_8.3)
(28) arag Do(AE)(cc_54.2) = Cc(AE)(mag_10.4)
(30) arag Do(AE)(cc_54.2) = Cc(AE)(mag_12.5)
(33) arag Do(AE)(cc_54.2) = Cc(AE)(mag_14.6)
(37) arag Do(AE)(cc_56.2) = Cc(AE)(mag_14.6)
(40) arag Do(AE)(cc_56.2) = Cc(AE)(mag_16.7)

Note that each segment of the same univariant curve differs from the others for the composition of one phase. This implies that the composition of solid solutions (Mg-calcite, dolomite and magnesite) changes along each univariant curve (as in all P-T projections involving solid solutions!).

(4) Comparing T-X sections and P-T projections

You can now compare the P-T projection with the T-XMgO sections obtained in Ex. 6.

Note that the two types of diagram provide the same information, but in different way.

In the **P-T projection**, the solid solutions compositional information is somehow "hidden": you can understand how solid solutions change their composition as a function of P and T by carefully analysing each segment of the univariant curves.

In the **isobaric T-X sections**, solid solutions compositions are explicitly indicated, but you need more than one diagram to understand how these compositions change as a function of pressure.

Ex. 8

Ex. 8 – P-T pseudosection for a METAPELITE in the KFMASH system

This exercise explains how to calculate a P-T pseudosection for a metapelite sample, in the simplified KFMASH system. The problem is a bit more complex than Ex. 4, because it involves SOLID SOLUTIONS. The influence of other components (Na_2O, CaO and MnO) will be considered in the next exercise (Ex. 9).
At the end, some practical tips for redrawing the PerpleX outputs are given.

This exercise is based on the paper by Tinkham et al. (2001) [Geol. Mat. Res., 3, 1-42]. The modelled sample is AWBZ (see Table 1 and their Fig. 3).

Total bulk composition (mol%; SiO2 in excess):
Al2O3=37.99, FeO=21.93, MgO=19.59, MnO=0.42, CaO=4.95, Na2O=6.11, K2O=9.01
Bulk composition recalculated ignoring MnO, CaO and Na2O components:
Al2O3=42.92, FeO=24.77, MgO=22.13, K2O=10.18
T=425-700°C
P=1-10 kbar

(1) Definition of the problem (BUILD)

C:\PERPLEX\Perplex686>build

Perple_X version 6.8.6, source updated Jan 24, 2019.
Copyright (C) 1986-2019 James A D Connolly <www.perplex.ethz/copyright.html>.

NO is the default (blank) answer to all Y/N prompts

Enter a name for this project (the name will be used as the root for all output file names) [default = my_project]:
Ex8

The problem definition file will be named: ex8.dat

Enter thermodynamic data file name [default = hp02ver.dat]:
hp62ver.dat

Enter the computational option file name [default = perplex_option.dat]:
See: www.perplex.ethz.ch/perplex_options.html
[enter]

Reading Perple_X options from: perplex_option.dat

The current data base components are:
 Na2O MgO Al2O3 SiO2 K2O CaO TiO2 MnO FeO NiO ZrO2 Cl2 O2 H2O CO2 CuO Cr2O3 S2
F2
Transform them (Y/N)?

---

n

Specify computational mode:

    1 - Convex-Hull minimization

    2 - Constrained minimization on a 2d grid [default]

    3 - Constrained minimization on a 1d grid

    4 - Output pseudocompound data

    5 - 1-d Phase fractionation calculations

    6 - 0-d Infiltration-reactionation-fractionation

    7 - 2-d Phase fractionation (FRAC2D and TITRATE reactive transport models)

Use Convex-Hull minimization for Schreinemakers projections or phase diagrams with > 2 independent variables. Use constrained minimization for phase diagrams or phase diagram sections with < 3 independent variables.

2

Calculations with a saturated fluid (Y/N)?

y

Select the independent saturated fluid components:

 H2O CO2

Enter names, 1 per line, press <enter> 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

Calculations with saturated components (Y/N)?

Y

warning ver015 if you select > 1 saturated component, then the order you enter the components determines the saturation heirarchy and may effect your results (see Connolly 1990).

Select < 6 saturated components from the set:

Na2O MgO Al2O3 SiO2 K2O CaO TiO2 MnO FeO NiO ZrO2 Cl2 O2   CO2   CuO Cr2O3 S2   F2

Enter names, 1 per line, press <enter> to finish:

SiO2

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

N

Select thermodynamic components from the set:

Na2O MgO Al2O3 K2O CaO TiO2 MnO FeO NiO ZrO2 Cl2 O2 CO2 CuO Cr2O3 S2   F2

Enter names, 1 per line, press <enter> to finish:

MgO

Al2O3

K2O

FeO

Because the thermodynamic data file identifies: H2O as special components, you will be prompted next for the EoS to be used for the corresponding composants and mixtures thereof. To override this behavior, e.g., to use a generic hybrid fluid EoS, delete the special_component section from the thermodynamic data file header.

Select fluid equation of state:
  0 - X(CO2) H2O-CO2 Modified Redlich-Kwong (MRK) DeSantis et al 74
  1 - X(CO2) H2O-CO2 HSMRK Kerrick & Jacobs 81
  2 - X(CO2) H2O-CO2 MRK hybrid-EoS*
  5 - X(CO2) H2O-CO2 CORK Holland & Powell 91, 98
  8 - f(O2/CO2) C-buffered COH MRK hybrid-EoS*
  10 - X(O) C-buffered COH MRK hybrid-EoS Connolly & Cesare 93*
  12 - X(O)-f(S2) C-buffered COHS MRK hybrid-EoS Connolly & Cesare 93*
  13 - X(H2) H2O-H2 MRK hybrid-EoS*
  14 - X(CO2) H2O-CO2 Pitzer & Sterner 94; Holland & Powell mixing 03
  15 - X(H2) H2O-H2 low T MRK hybrid-EoS*
  16 - X(O) H-O MRK hybrid-EoS*
  17 - X(O)-f(S2) H-O-S MRK hybrid-EoS*
  19 - X(O)-X(S) C-buffered COHS MRK hybrid-EoS Connolly & Cesare 93*
  20 - X(O)-X(C) COHS MRK hybrid-EoS Connolly & Cesare 93*
  24 - f(O2/CO2)-N/C C-buffered COHN MRK hybrid-EoS*
  25 - X(CO2)-X(NaCl) H2O-CO2-NaCl Aranovich et al 10
  26 - X(O) O-Si MRK Connolly 16
  27 - X(O)-X(C) C-O-H MRK hybrid-EoS*

*Hybrid EoS use the following pure species EoS, to change these associations modify the hybrid_EoS keywords in the perplex_option file:
    H2O - PSEoS Pitzer & Sterner 1994
    CO2 - PSEoS Pitzer & Sterner 1994
    CH4 - HSMRK Kerrick & Jacobs 1981
5

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

Select x-axis variable:
    1 - P(bar)
    2 - T(K)
    3 - Y(CO2)
    4 - Composition X(C1)* (user defined)
*Although only one component is specified for the Y(CO2)   phase, its equation of state permits use of its compositional variable:
*X(C1) can not be selected as the y-axis variable
2

Enter minimum and maximum values, respectively, for: T(K)
698
973

Select y-axis variable:

    2 - P(bar)

    3 - Y(CO2)

2

Enter minimum and maximum values, respectively, for: P(bar)

1000

10000

Specify sectioning value for: Y(CO2)

0

For gridded minimization, grid resolution is determined by the number of levels (grid_levels) and the resolution at the lowest level in the X- and Y-directions (x_nodes and y_nodes) these parameters are currently set for the exploratory and autorefi ne cycles as follows:

stage   grid_levels xnodes ynodes   effective resolution

exploratory   1   60   60   60 x 60 nodes

auto-refine   4   60   60   473 x 473 nodes

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

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

All thermodynamic components must be constrained, constrain saturated components also (Y/N)?

N

Specify component amounts by mass (Y/N)?

N

The amounts you enter next need not be normalized; regardless of units, they define the molar amount of the system

Enter the molar amounts of the components:

 MgO   Al2O3 K2O FeO

for the bulk composition of interest:

22.13

42.92

10.18

24.77

Output a print file (Y/N)?

Y

Exclude pure and/or endmember phases (Y/N)?

Y

Do you want to be prompted for phases (Y/N)?

N

Enter names, 1 per line, press <enter> to finish:

mic

In the metapelitic system, Kfs mostly derives from the breakdown of white mica at relatively high-T, therefore you should consider the high-T sanidine (san) end-member rather than microcline (mic).

Include solution models (Y/N)?

y

Enter solution model file name [default = solution_model.dat]:

[enter]

…

Select models from the following list, enter 1 per line, press <enter> to finish
clinopyroxene models: Cpx(H)   Augite(G) Cpx(JH)
clinoamphibole models: cAmph(G) Cumm   cAmph(DP) cAmph(G)_I
liquid models: melt(H)   melt(G)   Melt(JH) melt(W)   melt(HP)
chlorite models: Chl(W)   Chl(HP)   Chl(LWV)
olivine models: O(JH)   O(SG)   O(HP)   O(HPK)   O(stx)

            O(stx7)   O(stx8)
spinel models: Sp(JH)   GaHcSp   Sp(JR)   Sp(GS)   Sp(HP)   Sp(stx)   CrSp   Sp(stx7) Sp(WPC)   Sp(stx8)
garnet models: Grt(JH)   Gt(W)   CrGt   Gt(MPF)   Gt(B)   Gt(GCT)   Gt(HP)   Gt(EWHP) Gt(WPH)   Gt(stx)
            Gt(stx8) Gt(WPPH) ZrGt(KP) Maj
orthopyroxene models: Opx(JH)   Opx(W)   Opx(HP)   CrOpx(HP) Opx(stx)   Opx(stx8)
white-mica models: Mica(W)   Pheng(HP) Mica(CF) Mica(CHA1) Mica(CHA) Mica+(CHA) Mica(SGH)
chloritoid models: Ctd(W)   Ctd(HP)   Ctd(SGH)
staurolite models: St(W)   St(HP)
biotite models: Bi(W)   Bio(TCC) Bio(WPH) Bio(HP)
cordierite models: Crd(W)   hCrd
sapphirine models: Sa(WP)   Sapp(TP) Sapp(HP) Sapp(KWP)
carpholite models: Carp   Carp(M)   Carp(SGH)
sudoite models: Sud(Livi) Sud   Sud(M)
orthoamphibole models: Anth   oAmph(DP) o-Amph
stilpnomelane models: Stlp
alphabet-phase models: A-phase
clinohumite models: Chum
brucite models: B
aqueous_electrolyte model WADDAH
wadleysite models: Wad
ringwoodite models: Ring   Ring(H)
wuestite models: Wus
ilmenite models: Aki
perovskite models: Pv
High pressure garnet mode Gt(H)
ferropericlase models: Fper(H)
MgSi Perovskite models: Mpv(H)
CaSi Perovskite models: Cpv(H)
Corundum models: Cor(H)
Akimotoite models: Aki(H)
wadsleyite models: Wad(H)
HP_clinopyroxene models: Hpx(H)
talc models: T

serpentine models: Atg(PN)

For details on these models see:www.perplex.ethz.ch/perplex_solution_model_glossary.html or read the commentary in the solution model file.

Chl(W)

Bi(W)

Mica(W)

Gt(W)

Ctd(W)

St(W)

Crd(W)

Enter calculation title:

Ex8

(2) Doing the calculation (VERTEX)

Run VERTEX to make the calculation:

C:\PERPLEX\Perplex686>vertex

Perple_X version 6.8.6, source updated Jan 24, 2019.
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Enter the project name (the name assigned in BUILD) [default = my_project]:
Ex8

Reading problem definition from file: ex8.dat
Reading thermodynamic data from file: hp62ver.dat
Reading solution models from file: solution_model.dat
Writing print output to file: ex8.prn
Writing plot output to file: ex8.plt
Writing bulk composition plot output to file: ex8.blk
Reading Perple_X options from: perplex_option.dat
Writing auto refine summary to file: not requested
Writing pseudocompound glossary to file: not requested
Writing Perple_X option summary to file: not requested

Perple_X version 6.8.6, source updated Jan 24, 2019.
Copyright (C) 1986-2019 James A D Connolly <www.perplex.ethz/copyright.html>.

Perple_X computational option settings for VERTEX:
    Keyword: Value: Permitted values [default]:
  Auto-refine options:
    auto_refine   aut   off manual [auto]
  Free energy minimization options:
    final_resolution:
      exploratory stage   0.1E-1   [1e-2], target value, see actual values below
      auto-refine stage   0.1E-2   [1e-3], target value, see actual values below
    resolution_factor   2   >= 2 [2]

```
refinement_points       6       [aut] or 1->12; aut = automatic
solvus_tolerance_II   aut       0->1 [0.2]
global_reach_increment  0       >= 0 [0]
reach_increment_switch  on      [on] off all
zero_mode           0.1E-05   0->1 [1e-6]; < 0 => off
2D grid options:
 x_nodes           40 / 60   [20/40], >0, <2048; effective x-resolution   40 / 473 nodes
 y_nodes           40 / 60   [20/40], >0, <2048; effective y-resolution   40 / 473 nodes
 grid_levels        1 / 4    [1/4], >0, <10
 linear_model         on     off [on]
Solution subdivision options:
 initial_resolution:
   exploratory stage    0.0625    0->1 [1/16], 0 => off
   auto-refine stage    0.0208    0->1 [1/48 ], 0 => off
 stretch_factor       0.0020    >0 [2d-3]
 subdivision_override   off     [off] lin str
 hard_limits         off     [off] on
 refine_endmembers    F       [F] T
Thermodynamic options:
 solvus_tolerance     aut     [aut] or 0->1; aut = automatic, 0 => p=c pseudocompounds, 1 => homogenize
 T_stop (K)          0.0     [0]
 T_melt (K)          873.0    [873]
 order_check         on      off [on]
 approx_alpha        T       [T] F
 Anderson-Gruneisen    F       [F] T
 speciation_factor     100.    >10 [100] speciation precision = final resolution/speciation_factor
 speciation_max_it     100      [100]
 hybrid_EoS_H2O       4      [4] 0-2, 4-7
 hybrid_EoS_CO2       4      [4] 0-4, 7
 hybrid_EoS_CH4       0      [0] 0-1, 7
 aq_bad_results       err     [err] 101, 102, 103, ignore
 aq_lagged_speciation  F       [F] T
 aq_ion_H+          T       [T] F => use OH-
 aq_oxide_components   F       [F] T
 aq_solvent_solvus    T       [T] F
 aq_vapor_epsilon     1.0      [1.]
Input/Output options:
 dependent_potentials  off     off [on]
 pause_on_error       T       [T] F
 auto_exclude        T       [T] F
 logarithmic_p        F       [F] T
 bad_number         NaN      [NaN]
 interim_results      aut     [auto] off manual
Information file output options:
 option_list_files    F       [F] T; echo computational options
 pseudocompound_file   T       [F] T; echo static pseudocompound compositions
 auto_refine_file     F       [F] T; echo auto-refine compositions
Worst case (Cartesian) compositional resolution (mol):
 Exploratory stage:  0.521E-2
 Auto-refine stage:  0.868E-3
Adapative minimization will be done with:
```

4 iterations in the exploratory stage

5 iterations in the autorefine stage

To change these options see: www.perplex.ethz.ch/perplex_options.html

…

warning ver114 the following endmembers are missing for Chl(W)

  ff3cli   f3clin   mnchl

warning ver050 reformulating prismatic solution: Chl(W)   because of missing endmembers.

(reformulation can be controlled explicitly by excluding additional endmembers).

  2597 pseudocompounds generated for: Chl(W)

warning ver114 the following endmembers are missing for Gt(W)

  spss   gr   fmn_i   fkho_i   kho1   andr_i

warning ver050 reformulating prismatic solution: Gt(W)   because of missing endmembers.

(reformulation can be controlled explicitly by excluding additional endmembers).

   15 pseudocompounds generated for: Gt(W)

warning ver114 the following endmembers are missing for Mica(W)

  pa   ma1_dqf fmu

   150 pseudocompounds generated for: Mica(W)

warning ver114 the following endmembers are missing for Ctd(W)

  ctdo

   15 pseudocompounds generated for: Ctd(W)

warning ver114 the following endmembers are missing for St(W)

  mstt   msto   mnst

   15 pseudocompounds generated for: St(W)

warning ver114 the following endmembers are missing for Bi(W)

  ffbi_i   fbi   ftbi_i   tbi   mnbi

warning ver050 reformulating prismatic solution: Bi(W)   because of missing endmembers.

(reformulation can be controlled explicitly by excluding additional endmembers).

   286 pseudocompounds generated for: Bi(W)

warning ver114 the following endmembers are missing for Crd(W)

  mncrd   hmncrd_i

warning ver050 reformulating prismatic solution: Crd(W)   because of missing endmembers.

(reformulation can be controlled explicitly by excluding additional endmembers).

   286 pseudocompounds generated for: Crd(W)

Total number of pseudocompounds: 3364

This is the beginning of the EXPLORATORY COMPUTATIONAL STAGE

** Starting exploratory computational stage **

 2.5% done with low level grid.

 5.0% done with low level grid.

 7.5% done with low level grid.

 10.0% done with low level grid.

 12.5% done with low level grid.

 15.0% done with low level grid.

 17.5% done with low level grid.

20.0% done with low level grid.
22.5% done with low level grid.
25.0% done with low level grid.
27.5% done with low level grid.
30.0% done with low level grid.
32.5% done with low level grid.
35.0% done with low level grid.
37.5% done with low level grid.
40.0% done with low level grid.
42.5% done with low level grid.
45.0% done with low level grid.
47.5% done with low level grid.
50.0% done with low level grid.
52.5% done with low level grid.
55.0% done with low level grid.
57.5% done with low level grid.
60.0% done with low level grid.
62.5% done with low level grid.
65.0% done with low level grid.
67.5% done with low level grid.
70.0% done with low level grid.
72.5% done with low level grid.
75.0% done with low level grid.
77.5% done with low level grid.
80.0% done with low level grid.
82.5% done with low level grid.
85.0% done with low level grid.
87.5% done with low level grid.
90.0% done with low level grid.
92.5% done with low level grid.
95.0% done with low level grid.
97.5% done with low level grid.
100.0% done with low level grid.

Compositions for prismatic model: Chl(W)
  Simplex 1
    Composition   Minimum   Maximum
      1   0.17188   0.65104
      2   0.0000   0.0000
  Simplex 2
    Composition   Minimum   Maximum
      1   0.34896   0.53140

Endmember fractions for model: Gt(W)
    Endmember   Minimum   Maximum
    alm   0.69271   0.88021

Endmember fractions for model: Mica(W)
    Endmember   Minimum   Maximum
    mu   0.85938   0.96354
    cel   0.20833E-01 0.88542E-01

Endmember fractions for model: Ctd(W)

Endmember	Minimum	Maximum
fctd	0.83333	0.91667

Endmember fractions for model: St(W)

Endmember	Minimum	Maximum
fst	0.60938	0.85417

Compositions for prismatic model: Bi(W)
 Simplex 1

Composition	Minimum	Maximum
1	0.36458	0.68229

 Simplex 2

Composition	Minimum	Maximum
1	0.13542	0.41146

Compositions for prismatic model: Crd(W)
 Simplex 1

Composition	Minimum	Maximum
1	0.28125	0.46338

 Simplex 2

Composition	Minimum	Maximum
1	0.33333	0.65625

The failure rate during speciation (order-disorder) calculations is   0.000% out of a total of   4161952. calculations.
Average number of iterations per speciation calculation: 4.3

Reading data for auto-refinement from file: ex8.arf
    550 pseudocompounds generated for: Chl(W)
    11 pseudocompounds generated for: Gt(W)
    29 pseudocompounds generated for: Mica(W)
     6 pseudocompounds generated for: Ctd(W)
    14 pseudocompounds generated for: St(W)
    255 pseudocompounds generated for: Bi(W)
    187 pseudocompounds generated for: Crd(W)
Total number of pseudocompounds: 1052

This is the beginning of the AUTO-REFINE STAGE
** Starting auto_refine computational stage **
 0.2% done with low level grid.
 1.9% done with low level grid.
 3.6% done with low level grid.
 5.3% done with low level grid.
 7.0% done with low level grid.
 8.7% done with low level grid.
 10.4% done with low level grid.
 12.1% done with low level grid.
 13.7% done with low level grid.
 15.4% done with low level grid.
 17.1% done with low level grid.
 18.8% done with low level grid.
 20.5% done with low level grid.

22.2% done with low level grid.
23.9% done with low level grid.
25.6% done with low level grid.
27.3% done with low level grid.
29.0% done with low level grid.
30.7% done with low level grid.
32.3% done with low level grid.
34.0% done with low level grid.
35.7% done with low level grid.
37.4% done with low level grid.
39.1% done with low level grid.
40.8% done with low level grid.
42.5% done with low level grid.
44.2% done with low level grid.
45.9% done with low level grid.
47.6% done with low level grid.
49.3% done with low level grid.
51.0% done with low level grid.
52.6% done with low level grid.
54.3% done with low level grid.
56.0% done with low level grid.
57.7% done with low level grid.
59.4% done with low level grid.
61.1% done with low level grid.
62.8% done with low level grid.
64.5% done with low level grid.
66.2% done with low level grid.
67.9% done with low level grid.
69.6% done with low level grid.
71.2% done with low level grid.
72.9% done with low level grid.
74.6% done with low level grid.
76.3% done with low level grid.
78.0% done with low level grid.
79.7% done with low level grid.
81.4% done with low level grid.
83.1% done with low level grid.
84.8% done with low level grid.
86.5% done with low level grid.
88.2% done with low level grid.
89.9% done with low level grid.
91.5% done with low level grid.
93.2% done with low level grid.
94.9% done with low level grid.
96.6% done with low level grid.
98.3% done with low level grid.
100.0% done with low level grid.

Beginning grid refinement stage.
  596 grid cells to be refined at grid level 2
    ...working (501 minimizations done)

...working (1002 minimizations done)
     refinement at level 2 involved   1273 minimizations
  4873 minimizations required of the theoretical limit of   14161
  1040 grid cells to be refined at grid level 3
     ...working (231 minimizations done)
warning ver042 an optimization failed due to numerical instability or because the phases of the system do not span its bulk composition.
   In the 1st case:
      increase (sic) final_resolution and/or
      increase resolution_factor and/or
      increase reach_increment and/or
      increase speciation_factor and/or
      increase speciation_max_it and/or
    see: www.perplex.ch/perplex_options.html for explanation.
   In the 2nd case: change the bulk composition or add phases.

warning ver333 You've got to ask yourself one question: Do I feel lucky? Well, do ya, punk?
     ...working (732 minimizations done)
     ...working (1234 minimizations done)
     ...working (1736 minimizations done)
     refinement at level 3 involved   1894 minimizations
  6767 minimizations required of the theoretical limit of   56169
  1799 grid cells to be refined at grid level 4
warning ver042 an optimization failed due to numerical instability or because the phases of the system do not span its bulk composition.
   In the 1st case:
      increase (sic) final_resolution and/or
      increase resolution_factor and/or
      increase reach_increment and/or
      increase speciation_factor and/or
      increase speciation_max_it and/or
    see: www.perplex.ch/perplex_options.html for explanation.
   In the 2nd case: change the bulk composition or add phases.
warning ver333 You've got to ask yourself one question: Do I feel lucky? Well, do ya, punk?
     ...working (343 minimizations done)
warning ver042 an optimization failed due to numerical instability or because the phases of the system do not span its bulk composition.
   In the 1st case:
      increase (sic) final_resolution and/or
      increase resolution_factor and/or
      increase reach_increment and/or
      increase speciation_factor and/or
      increase speciation_max_it and/or
    see: www.perplex.ch/perplex_options.html for explanation.
   In the 2nd case: change the bulk composition or add phases.
warning ver333 You've got to ask yourself one question: Do I feel lucky? Well, do ya, punk?
     ...working (845 minimizations done)
warning ver042 an optimization failed due to numerical instability or because the phases of the system do not span its bulk composition.
   In the 1st case:
      increase (sic) final_resolution and/or

increase resolution_factor and/or

increase reach_increment and/or

increase speciation_factor and/or

increase speciation_max_it and/or

see: www.perplex.ch/perplex_options.html for explanation.

In the 2nd case: change the bulk composition or add phases.

warning ver333 You've got to ask yourself one question: Do I feel lucky? Well, do ya, punk?

...working (1346 minimizations done)

...working (1848 minimizations done)

...working (2349 minimizations done)

...working (2850 minimizations done)

refinement at level 4 involved   3071 minimizations

9838 minimizations required of the theoretical limit of 224676

warning ver993 The compositions of the following solutions reached internal limits that were automatically relaxed:

Chl(W)

Crd(W)

Restriction during the auto-refine stage is usually insignificant. If desired, confirm by comparing the ranges below to those in the *.arf file.

NOTE: unintentional restrictions encountered during the exploratory stage may be problematic, refer to the output written at the end of the exploratory stage for relevant warnings.

Compositions for prismatic model: Chl(W)

Simplex 1

Composition	Minimum	Maximum
1	0.16059	0.66059
2	0.86806E-03	0.86806E-03

Simplex 2

Composition	Minimum	Maximum
1	0.32899	0.53072

Endmember fractions for model: Gt(W)

Endmember	Minimum	Maximum
alm	0.69444	0.87847

Endmember fractions for model: Mica(W)

Endmember	Minimum	Maximum
mu	0.86458	0.96615
cel	0.18229E-01	0.87674E-01

Endmember fractions for model: Ctd(W)

Endmember	Minimum	Maximum
fctd	0.82812	0.91580

Endmember fractions for model: St(W)

Endmember	Minimum	Maximum
fst	0.60417	0.85677

Compositions for prismatic model: Bi(W)

Simplex 1

Composition	Minimum	Maximum
1	0.36285	0.68207

Simplex 2
  Composition Minimum   Maximum
     1   0.16059   0.41059

Compositions for prismatic model: Crd(W)
  Simplex 1
    Composition Minimum   Maximum
     1   0.26823   0.46181
  Simplex 2
    Composition Minimum   Maximum
     1   0.32552   0.65365

The failure rate during speciation (order-disorder) calculations is   0.000% out of a total of   14191024. calculations.
Average number of iterations per speciation calculation: 6.3

At the end of the calculation, a number of new files appear in the Perple_X folder. The most useful are the ***.prn and the ***.plt files (i.e. the text file and the plot file).

(3) Plotting the calculated phase diagram (PSSECT)

Run PSSECT to plot the calculated pseudosection:

C:\PERPLEX\Perplex686>pssect

Perple_X version 6.8.6, source updated Jan 24, 2019.
Copyright (C) 1986-2019 James A D Connolly <www.perplex.ethz/copyright.html>.

Enter the project name (the name assigned in BUILD) [default = my_project]:
Ex8

Reading Perple_X options from: perplex_option.dat

Perple_X plot options are currently set as:
  Keyword: Value: Permitted values [default]:
  axis_label_scale   1.20   [1.2] (rel)
  bounding_box :
                0   [0] x-min (pts)
                0   [0] y-min (pts)
              800   [800] x-length (pts)
              800   [800] y-length (pts)
  field_fill   T   [T] F
  field_label   T   [T] F
  field_label_scale   0.75   [0.72] (rel)
  font   Helvetica
  grid   F   [F] T
  half_ticks   T   [T] F
  line_width   1.00   0-99 [1.] (pts)
  picture_transformation :
              0.180   [0.18] x-scale (rel)
              0.180   [0.18] y-scale (rel)

130.   [0.18] x-translation (pts)
                220.   [0.18] y-translation (pts)
                0.00   [0.0] rotation (deg)
    plot_aspect_ratio   1.000   [1.0] x_axis_length/y_axis_length
    replicate_label   0.250   0->1 [0.025]
    splines   T   [T] F
    tenth_ticks   F   [F] T
    text_scale   1.000   [1.] (rel)
To change these options edit or create the plot option file
See: www.perplex.ethz.ch/perplex_plot_options.html

PostScript will be written to file: ex8.ps

Modify the default plot (y/n)?

n

Quartz and H_2O are in excess.

In the calculated pseudosection, field assemblages have different variances. Fields with the same grey colour have the same variance. Colour code is as follows: white = 2-variant fields, light grey = 3-variant fields, medium grey = 4-variant fields and so on. **Darker is the colour, higher is the variance (and lower is the number of phases!).**

(4) PRACTICAL TIPS FOR RE-DRAWING THE PERPLE_X OUTPUTS

In most cases, you should re-draw the final output in order to obtain a result that can be published. When re-drawing a pseudosection, be careful to not introduce topological errors.

General rules are:

(1) **Fields with the same variance should be indicated with the same colour.**

Remember that: F= C – P + 2. In this case: C = 9 (MnNKCFMASH)

Therefore, fields characterized by 9 phases (P=9; white fields in the pseudosection) are di-variant (F=9-9+2); fields with 8 phases (light grey) are tri-variant and so on.

(2) **in a point cannot converge more than 4 lines**

(3) **2 fields with the same variance n (i.e. with the same n° of phases) are always separated by a (n+1) or (n-1)-variant field, except when they are separated by a true univariant curve.**

(4) **Lines between fields always mark the APPEARANCE or DISAPPEARANCE of a phase**

Variance of each field is reported in brackets. The thick black lines are true univariant reactions.

+Qz + H₂O

The phase-in boundaries are reported with different colours for each phase.

(5) Calculating ISOMODES (WERAMI)

This section explains how to calculate the variation in the modal amounts of each mineral phase (vol%), for the modelled pseudosection.

C:\PERPLEX\Perplex686>werami

Perple_X version 6.8.6, source updated Jan 24, 2019.
Copyright (C) 1986-2019 James A D Connolly <www.perplex.ethz/copyright.html>.

Enter the project name (the name assigned in BUILD) [default = my_project]:
Ex8

Reading Perple_X options from: perplex_option.dat
Writing Perple_X option summary to file: not requested

Perple_X version 6.8.4, source updated Sept 30, 2018.
Copyright (C) 1986-2018 James A D Connolly <www.perplex.ethz/copyright.html>.

Perple_X computational option settings for WERAMI:
  Keyword: Value: Permitted values [default]:
 Input/Output options:
  aqueous_output   T   [F] T
  aqeuous_species   20   [20] 0-100
  aq_solvent_composition y   [y] m: y => mol fraction, m => molality
  aq_solute_composition m   y [m]: y => mol fraction, m => molality
  spreadsheet   T   [F] T
  logarithmic_p   F   [F] T
  bad_number   NaN   [NaN]
  composition_constant F   [F] T
  composition_phase   mol   [mol] wt
  composition_system   wt   [wt] mol
  proportions   vol   [vol] wt mol
  absolute   F   [F] T
  cumulative   F   [F] T
  fancy_cumulative_modes F   [F] T
  interpolation   on   [on] off
  melt_is_fluid   F   [F] T
  solution_names   abb   [model] abbreviation full
  species_output   T   [T] F
  species_Gibbs_energies F   [F] T
  seismic_output   som   [some] none all
  pause_on_error   T   [T] F
  poisson_test   F   [F] T
  auto_exclude   T   [T] F
 Information file output options:
  option_list_files   F   [F] T; echo computational options
 Thermodynamic options:
  approx_alpha   T   [T] F

```
  Anderson-Gruneisen    F      [F] T
  hybrid_EoS_H2O        1      [7] 0-2, 4-8
  hybrid_EoS_CO2        4      [7] 0-4
  hybrid_EoS_CH4        4      [1] 0-1
  fd_expansion_factor   2.0    >0 [2.]
  finite_difference_p   0.1D+05   >0 [1d4]; fraction = 0.1D-02   [1d-2]
 Seismic velocity options:
  bounds              VRH     [VRH] HS
  vrh/hs_weighting    0.5     [0.5] 0->1
  explicit_bulk_modulus  T    [F] T
  poisson_ratio       on      [on] all off; Poisson ratio = 0.35
To change these options see: www.perplex.ethz.ch/perplex_options.html
```

Select operational mode:
  1 - properties at specified conditions
  2 - properties on a 2d grid
  3 - properties along a 1d path
  4 - as in 3, but input from file
  0 – EXIT
2

Select a property [enter 0 to finish]:
  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 - Composition (Mol, Mass, or Wt%) of the system
  7 - Mode (Vol, Mol, or Wt proportion) of a phase
  8 - Composition (Mol, Mass, or Wt%) of a solution phase
  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-system)
 21 - Poisson ratio
 22 - Molar Volume (J/bar)
 23 - Dependent potentials (J/mol, bar, K)
 24 - Assemblage Index
 25 - Modes of all phases
 26 - Sound velocity T derivative (km/s/K)
 27 - P-wave velocity T derivative (km/s/K)
 28 - S-wave velocity T derivative (km/s/K)

29 - Adiabatic bulk modulus T derivative (bar/K)

30 - Shear modulus T derivative (bar/K)

31 - Sound velocity P derivative (km/s/bar)

32 - P-wave velocity P derivative (km/s/bar)

33 - S-wave velocity P derivative (km/s/bar)

34 - Adiabatic bulk modulus P derivative (unitless)

35 - Shear modulus P derivative (unitless)

36 - All phase &/or system properties

37 - Absolute amount (Vol, Mol, or Wt) of a phase

38 - Multiple property output

39 - Heat capacity ratio (Cp/Cv)

40 - Lagged or back-calculated aqueous solute chemistry

7

Enter solution or compound (left justified):

Gt(W)

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

n

Fractions are Wt, Vol, or Mol depending on the perplex_option.dat proportions keyword.

Mode can be computed as vol%, mol% or wt%. The default value is vol%. You can control this parameter modifying the "proportion" keyword in the perplex_option.dat file

Select a property [enter 0 to finish]:

7

Enter solution or compound (left justified):

Chl(W)

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

n

Fractions are Wt, Vol, or Mol depending on the perplex_option.dat proportions keyword.

Select a property [enter 0 to finish]:

7

Enter solution or compound (left justified):

Ctd(W)

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

n

Fractions are Wt, Vol, or Mol depending on the perplex_option.dat proportions keyword.

Select a property [enter 0 to finish]:

7

Enter solution or compound (left justified):

St(W)

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

n

Fractions are Wt, Vol, or Mol depending on the perplex_option.dat proportions keyword.

Select a property [enter 0 to finish]:

7

Enter solution or compound (left justified):

Mica(W)

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

n

Fractions are Wt, Vol, or Mol depending on the perplex_option.dat proportions keyword.

Select a property [enter 0 to finish]:

7

Enter solution or compound (left justified):

Bi(W)

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

n

Fractions are Wt, Vol, or Mol depending on the perplex_option.dat proportions keyword.

Select a property [enter 0 to finish]:

7

Enter solution or compound (left justified):

Crd(W)

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

n

Fractions are Wt, Vol, or Mol depending on the perplex_option.dat proportions keyword.

Select a property [enter 0 to finish]:

7

Enter solution or compound (left justified):

san

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

n

Fractions are Wt, Vol, or Mol depending on the perplex_option.dat proportions keyword.

Select a property [enter 0 to finish]:

7

Enter solution or compound (left justified):

ky

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

n

Fractions are Wt, Vol, or Mol depending on the perplex_option.dat proportions keyword.

Select a property [enter 0 to finish]:

7

Enter solution or compound (left justified):

sill

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

n

Fractions are Wt, Vol, or Mol depending on the perplex_option.dat proportions keyword.

Select a property [enter 0 to finish]:

7

Enter solution or compound (left justified):

and

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

n

Fractions are Wt, Vol, or Mol depending on the perplex_option.dat proportions keyword.

Select a property [enter 0 to finish]:

0

Change default variable range (y/n)?

n

Select the grid resolution (to use an arbitrary grid set sample_on_grid to F):
   1 - 60 x 60 nodes
   2 - 119 x 119 nodes
   3 - 237 x 237 nodes
   4 - 473 x 473 nodes [default]

4

…

…

Output has been written to the 2d tab format file: ex8_1.tab

2d tab format files can be processed with:
    PSTABLE - a Perple_X plotting program
    PERPLE_X_PLOT - a MATLAB plotting script
    PYWERAMI - petrol.natur.cuni.cz/~ondro/pywerami:home
    spread-sheet programs, e.g., EXCEL
for details on tab format refer to:
    perplex.ethz.ch/faq/perple_x_tab_file_format.txt

Select operational mode:
   1 - properties at specified conditions
   2 - properties on a 2d grid
   3 - properties along a 1d path
   4 - as in 3, but input from file
   0 - EXIT

0

At the end, you have a new file (ex8_1.tab) in the Perple_X folder.

(6) Calculating ISOPLETHS (WERAMI)

This section explains how to calculate COMPOSITIONAL ISOPLETHS for specific phases.

In this example, the XMg (Mg/Mg+Fe) for chloritoid, staurolite, garnet and biotite is calculated.

C:\PERPLEX\Perplex686>werami

Perple_X version 6.8.6, source updated Jan 24, 2019.
Copyright (C) 1986-2019 James A D Connolly <www.perplex.ethz/copyright.html>.

Enter the project name (the name assigned in BUILD) [default = my_project]:
Ex8

Reading Perple_X options from: perplex_option.dat
Writing Perple_X option summary to file: not requested

Perple_X version 6.8.6, source updated Jan 24, 2019.
Copyright (C) 1986-2019 James A D Connolly <www.perplex.ethz/copyright.html>.

Perple_X computational option settings for WERAMI:
    Keyword: Value: Permitted values [default]:
  Input/Output options:
    aqueous_output   T   [F] T
    aqeuous_species   20   [20] 0-100
    aq_solvent_composition y   [y] m: y => mol fraction, m => molality
    aq_solute_composition m   y [m]: y => mol fraction, m => molality
    spreadsheet   T   [F] T
    logarithmic_p   F   [F] T
    bad_number   NaN   [NaN]
    composition_constant F   [F] T
    composition_phase   mol   [mol] wt
    composition_system   wt   [wt] mol
    proportions   vol   [vol] wt mol
    absolute   F   [F] T
    cumulative   F   [F] T
    fancy_cumulative_modes F   [F] T
    interpolation   on   [on] off
    melt_is_fluid   F   [F] T
    solution_names   abb   [model] abbreviation full
    species_output   T   [T] F
    species_Gibbs_energies F   [F] T
    seismic_output   som   [some] none all
    pause_on_error   T   [T] F
    poisson_test   F   [F] T
    auto_exclude   T   [T] F
  Information file output options:
    option_list_files   F   [F] T; echo computational options
  Thermodynamic options:

```
approx_alpha        T      [T] F
Anderson-Gruneisen  F      [F] T
hybrid_EoS_H2O      1      [7] 0-2, 4-8
hybrid_EoS_CO2      4      [7] 0-4
hybrid_EoS_CH4      4      [1] 0-1
fd_expansion_factor 2.0    >0 [2.]
finite_difference_p 0.1D+05  >0 [1d4]; fraction = 0.1D-02  [1d-2]
```
Seismic velocity options:
```
bounds              VRH    [VRH] HS
vrh/hs_weighting    0.5    [0.5] 0->1
explicit_bulk_modulus T    [F] T
poisson_ratio       on     [on] all off; Poisson ratio = 0.35
```
To change these options see: www.perplex.ethz.ch/perplex_options.html

Select operational mode:
  1 - properties at specified conditions
  2 - properties on a 2d grid
  3 - properties along a 1d path
  4 - as in 3, but input from file
  0 - EXIT
2

Select a property [enter 0 to finish]:
  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 - Composition (Mol, Mass, or Wt%) of the system
  7 - Mode (Vol, Mol, or Wt proportion) of a phase
  8 - Composition (Mol, Mass, or Wt%) of a solution phase
  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-system)
  21 - Poisson ratio
  22 - Molar Volume (J/bar)
  23 - Dependent potentials (J/mol, bar, K)
  24 - Assemblage Index
  25 - Modes of all phases
  26 - Sound velocity T derivative (km/s/K)
  27 - P-wave velocity T derivative (km/s/K)

28 - S-wave velocity T derivative (km/s/K)

29 - Adiabatic bulk modulus T derivative (bar/K)

30 - Shear modulus T derivative (bar/K)

31 - Sound velocity P derivative (km/s/bar)

32 - P-wave velocity P derivative (km/s/bar)

33 - S-wave velocity P derivative (km/s/bar)

34 - Adiabatic bulk modulus P derivative (unitless)

35 - Shear modulus P derivative (unitless)

36 - All phase &/or system properties

37 - Absolute amount (Vol, Mol, or Wt) of a phase

38 - Multiple property output

39 - Heat capacity ratio (Cp/Cv)

40 - Lagged or back-calculated aqueous solute chemistry

8

Enter solution (left justified):

Gt(W)

Define the composition in terms of the species/endmembers of Gt(W)   (y/n)?

Answer no to define a composition in terms of the systems components. (e.g. MgO, FeO, etc.)

Answer yes to define a composition in terms of the solid solution end-members (e.g. Prp, Alm, etc.)

Units (mass or molar) are controlled by the composition keyword in perplex_option.dat.

Phase compositions can be computed as mol% or wt%. The default value is mol%. You can control this parameter modifying the "composition_phase" keyword in the perplex_option.dat file

n

Compositions are defined as a ratio of the form:

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

         n(j)   = molar amount of component j

         w(j)   = weighting factor of component j (usually 1)

How many components in the numerator of the composition (<13)?

We want to calculate the ratio Mg/(Mg+Fe), this means that we have one component in the numerator (MgO) and two components in the denominator (MgO + FeO)

1

Enter component indices and weighting factors for the numerator:

  1 - MgO

  2 - Al2O3

  3 - K2O

  4 - FeO

  5 - SiO2

  6 - H2O

The weighting factor corresponds to the number of cations in each component (e.g. for MgO the weighting factor is 1; for K2O the weighting factor is 2 etc.)

1

1

How many components in the denominator of the composition (<12)?

Enter zero to use the numerator as a composition.

2

Enter component indices and weighting factors for the denominator:

  1 - MgO

  2 - Al2O3

  3 - K2O

  4 - FeO

  5 - SiO2

  6 - H2O

1

1

4

1

The compositional variable is:

1.0 MgO

  divided by

1.0 MgO + 1.0 FeO

Change it (y/n)?

n

This composition will be designated: C[Gt(W)1]

Select a property [enter 0 to finish]:

8

Enter solution (left justified):

Ctd(W)

Define the composition in terms of the species/endmembers of Ctd(W)   (y/n)?

Answer no to define a composition in terms of the systems components.

Units (mass or molar) are controlled by the composition keyword in perplex_option.dat.

n

Compositions are defined as a ratio of the form:

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

       n(j)   = molar amount of component j

       w(j)   = weighting factor of component j (usually 1)

How many components in the numerator of the composition (<13)?

1

Enter component indices and weighting factors for the numerator:

  1 - MgO

  2 - Al2O3

  3 - K2O

  4 - FeO

  5 - SiO2

6 - H2O
1
1

How many components in the denominator of the composition (<12)?
Enter zero to use the numerator as a composition.
2

Enter component indices and weighting factors for the denominator:
   1 - MgO
   2 - Al2O3
   3 - K2O
   4 - FeO
   5 - SiO2
   6 - H2O
1
1
4
1

The compositional variable is:
1.0 MgO
   divided by
1.0 MgO + 1.0 FeO
Change it (y/n)?
n

This composition will be designated: C[Ctd(W)2]

Select a property [enter 0 to finish]:
8

Enter solution (left justified):
St(W)

Define the composition in terms of the species/endmembers of St(W)   (y/n)?
Answer no to define a composition in terms of the systems components.
Units (mass or molar) are controlled by the composition keyword in perplex_option.dat.
n

Compositions are defined as a ratio of the form:
   Sum {w(i)*n(i), i = 1, c1} / Sum {w(i)*n(i), i = c2, c3}
         n(j)   = molar amount of component j
         w(j)   = weighting factor of component j (usually 1)
How many components in the numerator of the composition (<13)?
1

Enter component indices and weighting factors for the numerator:

   1 - MgO

   2 - Al2O3

   3 - K2O

   4 - FeO

   5 - SiO2

   6 - H2O

1

1

How many components in the denominator of the composition (<12)?

Enter zero to use the numerator as a composition.

2

Enter component indices and weighting factors for the denominator:

   1 - MgO

   2 - Al2O3

   3 - K2O

   4 - FeO

   5 - SiO2

   6 - H2O

1

1

4

1

The compositional variable is:

1.0 MgO

  divided by

1.0 MgO + 1.0 FeO

Change it (y/n)?

n

This composition will be designated: C[St(W)3]

Select a property [enter 0 to finish]:

8

Enter solution (left justified):

Bi(W)

Define the composition in terms of the species/endmembers of Bi(W)   (y/n)?

Answer no to define a composition in terms of the systems components.

Units (mass or molar) are controlled by the composition keyword in perplex_option.dat.

n

Compositions are defined as a ratio of the form:

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

     n(j)   = molar amount of component j

w(j)   = weighting factor of component j (usually 1)
How many components in the numerator of the composition (<13)?
1

Enter component indices and weighting factors for the numerator:
   1 - MgO
   2 - Al2O3
   3 - K2O
   4 - FeO
   5 - SiO2
   6 - H2O
1
1

How many components in the denominator of the composition (<12)?
Enter zero to use the numerator as a composition.
2

Enter component indices and weighting factors for the denominator:
   1 - MgO
   2 - Al2O3
   3 - K2O
   4 - FeO
   5 - SiO2
   6 - H2O
1
1
4
1

The compositional variable is:
1.0 MgO
   divided by
1.0 MgO + 1.0 FeO
Change it (y/n)?
n

This composition will be designated: C[Bi(W)4]

Select a property [enter 0 to finish]:
0

Change default variable range (y/n)?
n

Select the grid resolution (to use an arbitrary grid set sample_on_grid to F):
   1 -   60 x   60 nodes
   2 - 119 x 119 nodes

3 - 237 x 237 nodes
4 - 473 x 473 nodes [default]

4

…

Data ranges excluding values equal to bad_number (NaN) specified in perplex_option.dat:
   C[Gt(W)1]   C[Ctd(W)2]   C[St(W)3]   C[Bi(W)4]
min 0.121528   0.842014E-001 0.143229   0.318038
max 0.305556   0.171875   0.395833   0.637153
Output has been written to the 2d tab format file: ex8_2.tab

2d tab format files can be processed with:
   PSTABLE - a Perple_X plotting program
   PERPLE_X_PLOT - a MATLAB plotting script
   PYWERAMI - github.com/ondrolexa/pywerami
   spread-sheet programs, e.g., EXCEL
for details on tab format refer to:
   perplex.ethz.ch/perplex/faq/Perple_X_tab_file_format.txt

Select operational mode:
   1 - properties at specified conditions
   2 - properties on a 2d grid
   3 - properties along a 1d path
   4 - as in 3, but input from file
   0 - EXIT

0

At the end, you have a new file (ex8_2.tab) in the Perple_X folder.

(7) Plotting isomodes and compositional isopleths (PYWERAMI)

Use PYWERAMI to plot the calculated isomodes and compositional isopleths.

You can download Pywerami at this link from the Perple_X website (PyWerami - a free alternative to MatLab): https://petrol.natur.cuni.cz/~ondro/oldweb/pywerami:home
Install Pywerami on your pc.

Run PYWERAMI to plot isopleths and isomodes.

From Pywerami, open the .tab file.
Use the drop-down menu on the right to select the property you want to plot (e.g. Gt vol%, Gt(W)vo%)

You can modify the minimum and maximum values to be plotted, as well as the interval between the isopleths/isomodes.

You can save the image in .jpg or (**BETTER IF YOU WANT TO MODIFY THE FIGURE**) in .ps.

Ex. 9

Ex. 9 – P-T pseudosection for a METAPELITE in the MnNKCFMASH system

This exercise is intended to explore the influence of some minor components (Na₂O, CaO and MnO) on the topology of the pseudosection calculated for the metapelite sample investigated in Ex. 8.

This exercise is based on the paper by Tinkham et al. (2001) [Geol. Mat. Res., 3, 1-42]. The modelled sample is AWBZ (see Table 1 and their Fig. 5a).

Total bulk composition (mol%; SiO2 in excess):
Al2O3=37.99, FeO=21.93, MgO=19.59, MnO=0.42, CaO=4.95, Na2O=6.11, K2O=9.01
T=425-700°C
P=1-10 kbar

(1) Definition of the problem (BUILD)

Because the problem is the same as in Ex. 8, except for the addition of Na2O, CaO and MnO components **you can edit the ex8.dat input file** (remember to re-name the file as Ex9). Thus, the thermodynamic components are:

```
begin thermodynamic component list
Na2O  1 6.11000    0.00000    0.00000    molar amount
MgO   1 19.5900    0.00000    0.00000    molar amount
Al2O3 1 37.9900    0.00000    0.00000    molar amount
K2O   1 9.01000    0.00000    0.00000    molar amount
CaO   1 4.95000    0.00000    0.00000    molar amount
MnO   1 0.42000    0.00000    0.00000    molar amount
FeO   1 21.9300    0.00000    0.00000    molar amount
end thermodynamic component list
```

Adding Na2O and CaO additionally implies that the ternary feldspar (plagioclase + K-feldspar) solid solution model should be added to the calculation. Furthermore, end-members in the "feldspar" solution models are abh, an and san, respectively. Therefore, the ab and mic end-members should be excluded from the calculation, in order to not interfere with the abh and san end-members.

```
begin solution phase list
Chl(W)
Bi(W)
Mica(W)
Gt(W)
Ctd(W)
St(W)
Crd(W)
feldspar
end solution phase list
```

```
begin excluded phase list
ab
mic
end excluded phase list
```

(2) Doing the calculation (VERTEX)

Run VERTEX to make the calculation:

C:\PERPLEX\Perplex686>vertex

Perple_X version 6.8.6, source updated Jan 24, 2019.
Copyright (C) 1986-2019 James A D Connolly <www.perplex.ethz/copyright.html>.

Enter the project name (the name assigned in BUILD) [default = my_project]:
Ex9

…

(3) Plotting the calculated phase diagram (PSSECT)

Run PSSECT to plot the calculated pseudosection:

C:\PERPLEX\Perplex686>pssect

Perple_X version 6.8.6, source updated Jan 24, 2019.
Copyright (C) 1986-2019 James A D Connolly <www.perplex.ethz/copyright.html>.

Enter the project name (the name assigned in BUILD) [default = my_project]:
Ex9

Reading Perple_X options from: perplex_option.dat

Perple_X plot options are currently set as:
    Keyword: Value: Permitted values [default]:
    axis_label_scale   1.20   [1.2] (rel)
    bounding_box :
                0   [0] x-min (pts)
                0   [0] y-min (pts)
              800   [800] x-length (pts)
              800   [800] y-length (pts)
    field_fill   T   [T] F
    field_label   T   [T] F
    field_label_scale   0.75   [0.72] (rel)
    font   Helvetica
    grid   F   [F] T
    half_ticks   T   [T] F
    line_width   1.00   0-99 [1.] (pts)
    picture_transformation :
              0.180   [0.18] x-scale (rel)
              0.180   [0.18] y-scale (rel)
              130.   [0.18] x-translation (pts)
              220.   [0.18] y-translation (pts)
              0.00   [0.0] rotation (deg)
    plot_aspect_ratio   1.000   [1.0] x_axis_length/y_axis_length

```
replicate_label      0.250     0->1 [0.025]
splines         T        [T] F
tenth_ticks     F        [F] T
text_scale      1.000    [1.] (rel)
```
To change these options edit or create the plot option file
See: www.perplex.ethz.ch/perplex_plot_options.html

PostScript will be written to file: ex9.ps

Modify the default plot (y/n)?
N

Quartz and H2O are in excess.

Note that both plagioclase and K-feldspar are reported with the abbreviation "Fsp". Thus, fields containing two feldspars (Fsp Fsp) contain both plagioclase and K-feldspar, whereas those containing one feldspar (Fsp) can contain either plagioclase or K-feldspar. **To know which of the two feldspars is stable in a given field, use WERAMI option 1 (properties at specified conditions)**, e.g. at 753 K, 2800 bar:

Stable phases at:

        T(K)   = 753.000
        P(bar) = 2800.00
        Y(CO2) = 0.00000

Phase Compositions (molar proportions):

	wt %	vol %	mol %	mol	Na2O	MgO	Al2O3	K2O	CaO	MnO	FeO	SiO2	H2O
Chl	17.60	17.04	10.81	4.26	0.00000	2.55666	1.24760	0.00000	0.00000	0.05784	2.13791	2.75240	4.00000
Mica	31.65	31.91	30.62	12.1	0.06267	0.03038	1.44894	0.43586	0.00294	0.00000	0.02215	3.04960	1.00000
Bio	23.03	21.27	18.75	7.40	0.00000	1.12483	0.65563	0.50000	0.00000	0.02344	1.69611	2.84437	1.00000
Fsp	**27.72**	**29.78**	**39.82**	**15.7**	**0.34070**	**0.00000**	**0.65641**	**0.00289**	**0.31281**	**0.00000**	**0.00000**	**2.68719**	**0.00000**

Phase speciation (molar proportions):

Chl   daph: 0.46703, ames: 0.24846, afchl: 0.19936, clin: 0.27208, mnchl: 0.01157, och1: 0.00031, och2: -0.19882
Mica   mu: 0.81919, pa: 0.12535, ma1_dqf: 0.00294, cel: 0.03038, fcel: 0.02215
Bio   east: 0.15563, ann: 0.54813, phl: 0.23671, mnbi: 0.00781, obi: 0.05171
Fsp   abh: 0.68141, an: 0.31281, san: 0.00578

The feldspar stable at 753 K, 2800 bar is a plagioclase.

Ex.8 (KFMASH)

+Qz + H₂O is rendered as +Qz + H_2O

Legend (Ex.8): Als, Bt, Chl, Crd, Ctd, Grt, Kfs, Mu, St

Field labels: Chl Mu Ctd; Chl Grt Mu St; Grt Mu St Bt; Grt Mu Bt Als; Chl Mu St; Mu St Bt Als; Mu St Bt; Chl Mu; Bt Als Kfs; Mu Bt Als; Chl Mu Bt; Mu Bt Als Crd; Bt Crd Kfs; Bt Als Crd Kfs

Axes: P (kbar) 10.0, 8.2, 6.4, 4.6, 2.8, 1.0; T (°C) 425, 480, 535, 590, 645, 700

Ex. 9 (MnNCKFMASH)

+Qz +Bt +H₂O is rendered as +Qz +Bt +H_2O

Legend (Ex.9): Als, Bt, Chl, Crd, Grt, Kfs, Mu, Pa, Pl, St, Zo

Field labels: Chl Grt Mu Pa Zo; Grt Mu Pa Zo; Grt Mu Pa Pl; Chl Grt Mu Pa Pl; Grt Mu Pl; Chl Grt Mu Pl Zo; Chl Grt Mu Pl; Grt Mu St Pl; Chl Mu Pl Zo; Grt Pl Kfs Als; Chl Mu Pl; Grt Mu Pl Als; Grt Crd Pl Kfs; Crd Pl Kfs Als; Mu Crd Pl Als; Crd Pl Kfs; Mu Crd Pl

Axes: P (kbar) 10.0, 8.2, 6.4, 4.6, 2.8, 1.0; T (°C) 425, 480, 535, 590, 645, 700

Compare this pseudosection with that modelled in Ex. 8 (KFMASH system). Note that the introduction of Na₂O, CaO and MnO has the following consequences:

- **The garnet stability field is significantly enlarged toward low P and T with respect to the pseudosection of Ex. 8;**
- **Chloritoid is no more stable;**
- **The biotite stability field is significantly enlarged toward lower T (biotite is predicted to be stable in all the fields);**
- **Plagioclase is predicted to be stable in most of the fields;**
- **Zoisite appears at low T.**

Ex. 10

Ex. 10 – T-XMg pseudosection for a METAPELITE in the MnNKCFMASH system

This exercise is intended to explore the influence of bulk XMg [MgO/(MgO+FeO)] on the stability field of the main mineral assemblages, for the same metapelite sample investigated in Ex. 8 and 9.

The exercise provides the opportunity to calculate an isobaric T-X pseudosection (i.e. a phase diagram section with a compositional parameter on the horizontal axis).

This exercise is based on the paper by Tinkham et al. (2001) [Geol. Mat. Res., 3, 1-42]. The modelled sample is AWBZ (see Table 1 and their Fig. 10).

The T-XMg pseudosection is calculated at a fixed pressure of 3.5 kbar and for XMg ranging between 0 and 1. The XMg of the metapelite investigated in Ex. 9 is XMg=0.47.

The two bulk compositions to be used are (mol%; SiO2 in excess):
XMg=0: Al2O3=37.99, FeO=41.52, MgO=0.00, MnO=0.42, CaO=4.95, Na2O=6.11, K2O=9.01
XMg=1: Al2O3=37.99, FeO=000, MgO=41.52, MnO=0.42, CaO=4.95, Na2O=6.11, K2O=9.01
T=425-700°C
P=3.5 kbar
Use the same solid solution models used in Ex. 9

(1) Definition of the problem (BUILD)

C:\PERPLEX\Perplex686>build

Perple_X version 6.8.6, source updated Jan 24, 2019.
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NO is the default (blank) answer to all Y/N prompts

Enter a name for this project (the name will be used as the root for all output file names) [default = my_project]:
Ex10

The problem definition file will be named: ex10.dat

Enter thermodynamic data file name [default = hp02ver.dat]:
hp62ver.dat

Enter the computational option file name [default = perplex_option.dat]:
See: www.perplex.ethz.ch/perplex_options.html
[enter]

Reading computational options from: perplex_option.dat

The current data base components are:

Na2O MgO Al2O3 SiO2 K2O CaO TiO2 MnO FeO NiO ZrO2 Cl2 O2   H2O CO2 CuO Cr2O3 S2   F2
Transform them (Y/N)?
N

Specify computational mode:
    1 - Convex-Hull minimization
    2 - Constrained minimization on a 2d grid [default]
    3 - Constrained minimization on a 1d grid
    4 - Output pseudocompound data
    5 - 1-d Phase fractionation calculations
    6 - 0-d Infiltration-reactionation-fractionation
    7 - 2-d Phase fractionation (FRAC2D and TITRATE reactive transport models)
Use Convex-Hull minimization for Schreinemakers projections or phase diagrams with > 2 independent variables. Use constrained minimization for phase diagrams or phase diagram sections with < 3 independent variables.
2

Calculations with a saturated   FLUID (Y/N)?
Y

Select the independent saturated   FLUID components:
 H2O   CO2
Enter names, 1 per line, press <enter> 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

Calculations with saturated components (Y/N)?
Y
warning ver015 if you select > 1 saturated component, then the order you enter the components determines the saturation heirarchy and may effect your results (see Connolly 1990).

Na2O MgO Al2O3 SiO2 K2O CaO TiO2 MnO FeO NiO ZrO2 Cl2 O2   CO2 CuO Cr2O3 S2   F2
SiO2

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

Select thermodynamic components from the set:
Na2O MgO Al2O3 K2O CaO TiO2 MnO FeO NiO ZrO2 Cl2 O2 CO2 CuO Cr2O3 S2   F2
Enter names, 1 per line, press <enter> to finish:
Na2O
MgO
Al2O3
K2O
CaO

MnO
FeO

Because the thermodynamic data file identifies: H2O as special components, you will be prompted next for the EoS to be used for the corresponding composants and mixtures thereof. To override this behavior, e.g., to use a generic hybrid fluid EoS, delete the special_component section from the thermodynamic data file header.

Select fluid equation of state:
  0 - X(CO2) H2O-CO2 Modified Redlich-Kwong (MRK) DeSantis et al 74
  1 - X(CO2) H2O-CO2 HSMRK Kerrick & Jacobs 81
  2 - X(CO2) H2O-CO2 MRK hybrid-EoS*
  5 - X(CO2) H2O-CO2 CORK Holland & Powell 91, 98
  8 - f(O2/CO2) C-buffered COH MRK hybrid-EoS*
  10 - X(O) C-buffered COH MRK hybrid-EoS Connolly & Cesare 93*
  12 - X(O)-f(S2) C-buffered COHS MRK hybrid-EoS Connolly & Cesare 93*
  13 - X(H2) H2O-H2 MRK hybrid-EoS*
  14 - X(CO2) H2O-CO2 Pitzer & Sterner 94; Holland & Powell mixing 03
  15 - X(H2) H2O-H2 low T MRK hybrid-EoS*
  16 - X(O) H-O MRK hybrid-EoS*
  17 - X(O)-f(S2) H-O-S MRK hybrid-EoS*
  19 - X(O)-X(S) C-buffered COHS MRK hybrid-EoS Connolly & Cesare 93*
  20 - X(O)-X(C) COHS MRK hybrid-EoS Connolly & Cesare 93*
  24 - f(O2/CO2)-N/C C-buffered COHN MRK hybrid-EoS*
  25 - X(CO2)-X(NaCl) H2O-CO2-NaCl Aranovich et al 10
  26 - X(O) O-Si MRK Connolly 16
  27 - X(O)-X(C) C-O-H MRK hybrid-EoS*
*Hybrid EoS use the following pure species EoS, to change these associations modify the hybrid_EoS keywords in the perplex_option file:
    H2O - PSEoS Pitzer & Sterner 1994
    CO2 - PSEoS Pitzer & Sterner 1994
    CH4 - HSMRK Kerrick & Jacobs 1981
5

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

Select x-axis variable:
    1 - P(bar)
    2 - T(K)
    3 - Y(CO2)
    4 - Composition X_C1* (user defined)
*Although only one component is specified for the Y(CO2)   phase, its equation of state permits use of its compositional variable:
*X_C1 can not be selected as the y-axis variable
In this case, the x-axis variable is a composition (XMg)
4

Select y-axis variable:
    1 - P(bar)

2 - T(K)
    3 - Y(CO2)
    4 - Composition X_C2 (user defined)
2

Enter minimum and maximum values, respectively, for: T(K)
698
973

Specify sectioning value for: P(bar)
3500

Specify sectioning value for: Y(CO2)
0

For gridded minimization, grid resolution is determined by the number of levels (grid_levels) and the resolution at the lowest level in the X- and Y-directions (x_nodes and y_nodes) these parameters are currently set for the exploratory and autorefine cycles as follows:
stage   grid_levels xnodes ynodes   effective resolution
exploratory   1   60   60   60 x 60 nodes
auto-refine   4   60   60   473 x 473 nodes
To change these options edit or create the file perplex_option.dat
See: www.perplex.ethz.ch/perplex_options.html#grid_parameters

All thermodynamic components must be constrained, constrain saturated components also (Y/N)?
N

Specify component amounts by mass (Y/N)?
N

The amounts you enter next need not be normalized; regardless of units, they define the molar amount of the system

The bulk composition of the system will be computed as:
   C = C0*(1 - X_C1) + C1*X_C1
where X_C1 varies between 0 and 1, and C0 and C1 are the compositions specified next.

To compute bulk compositions as: C = C0 + C1*X_C1 change the computational option keyword closed_c_space.

Enter the molar amounts of the components:
 Na2O MgO Al2O3 K2O CaO MnO FeO
to define the composition C0
This corresponds to XMgO=0
6.11
0.00
37.99
9.01
4.95
0.42

41.52

Enter molar amounts of the components:
Na2O MgO Al2O3 K2O CaO MnO FeO
to define the composition C1
This corresponds to XMgO=1

6.11
41.52
37.99
9.01
4.95
0.42
0.00

Output a print file (Y/N)?
Y

…

Exclude pure and/or endmember phases (Y/N)?
Y

Do you want to be prompted for phases (Y/N)?
N

Enter names, 1 per line, press <enter> to finish:
mic
ab

Include solution models (Y/N)?
Y

Enter solution model file name [default = solution_model.dat] left justified, < 100 characters:
[return]

…

Select models from the following list, enter 1 per line, press <enter> to finish
clinopyroxene models: Cpx(H)   Augite(G) Cpx(JH)
clinoamphibole models: cAmph(G) Cumm   cAmph(DP) cAmph(G)_I
liquid models: melt(H)   melt(G)   Melt(JH) melt(W)   melt(HP)
chlorite models: Chl(W)   Chl(HP)   Chl(LWV)
olivine models: O(JH)   O(SG)   O(HP)   O(HPK)   O(stx)

            O(stx7)   O(stx8)
spinel models: Sp(JH)   GaHcSp   Sp(JR)   Sp(GS)   Sp(HP)   Sp(stx)   CrSp   Sp(stx7) Sp(WPC)   Sp(stx8)
garnet models: Grt(JH)   Gt(W)   CrGt   Gt(MPF)   Gt(B)   Gt(GCT)   Gt(HP)   Gt(EWHP) Gt(WPH)   Gt(stx)
            Gt(stx8) Gt(WPPH) ZrGt(KP)   Maj
orthopyroxene models: Opx(JH)   Opx(W)   Opx(HP)   CrOpx(HP) Opx(stx)   Opx(stx8)
white-mica models: Mica(W)   Pheng(HP) Mica(CF) Mica(CHA1) Mica(CHA) Mica+(CHA) Mica(SGH)
chloritoid models: Ctd(W)   Ctd(HP)   Ctd(SGH)

staurolite models: St(W)   St(HP)

biotite models: Bi(W)   Bio(TCC) Bio(WPH) Bio(HP)

cordierite models: Crd(W)   hCrd

sapphirine models: Sa(WP)   Sapp(TP) Sapp(HP) Sapp(KWP)

carpholite models: Carp   Carp(M)   Carp(SGH)

sudoite models: Sud(Livi) Sud   Sud(M)

orthoamphibole models: Anth   oAmph(DP) o-Amph

stilpnomelane models: Stlp

alphabet-phase models: A-phase

clinohumite models: Chum

brucite models: B

aqueous_electrolyte model WADDAH

wadleysite models: Wad

ringwoodite models: Ring   Ring(H)

wuestite models: Wus

ilmenite models: Aki

perovskite models: Pv

High pressure garnet mode Gt(H)

ferropericlase models: Fper(H)

MgSi Perovskite models: Mpv(H)

CaSi Perovskite models: Cpv(H)

Corundum models: Cor(H)

Akimotoite models: Aki(H)

wadsleyite models: Wad(H)

HP_clinopyroxene models: Hpx(H)

talc models: T

serpentine models: Atg(PN)

For details on these models see:www.perplex.ethz.ch/perplex_solution_model_glossary.html or read the commentary in the solution model file.

Chl(W)

Bi(W)

Mica(W)

Gt(W)

Ctd(W)

St(W)

Crd(W)

feldspar

Enter calculation title:

Ex10

(2) Doing the calculation (VERTEX)

Run VERTEX to make the calculation:

C:\PERPLEX\Perplex686>vertex

Perple_X version 6.8.6, source updated Jan 24, 2019.
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Enter the project name (the name assigned in BUILD) [default = my_project]:
Ex10

….

(3) Plotting the calculated phase diagram (PSSECT)

Run PSSECT to plot the calculated pseudosection:

C:\PERPLEX\Perplex686>pssect

Perple_X version 6.8.6, source updated Jan 24, 2019.
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Enter the project name (the name assigned in BUILD) [default = my_project]:
Ex10

Reading Perple_X options from: perplex_option.dat

Perple_X plot options are currently set as:
   Keyword: Value: Permitted values [default]:
   axis_label_scale   1.20   [1.2] (rel)
   bounding_box :
            0   [0] x-min (pts)
            0   [0] y-min (pts)
          800   [800] x-length (pts)
          800   [800] y-length (pts)
   field_fill   T   [T] F
   field_label   T   [T] F
   field_label_scale   0.75   [0.72] (rel)
   font   Helvetica
   grid   F   [F] T
   half_ticks   T   [T] F
   line_width   1.00   0-99 [1.] (pts)
   picture_transformation :
          0.180   [0.18] x-scale (rel)
          0.180   [0.18] y-scale (rel)
          130.   [0.18] x-translation (pts)
          220.   [0.18] y-translation (pts)
          0.00   [0.0] rotation (deg)
   plot_aspect_ratio   1.000   [1.0] x_axis_length/y_axis_length
   replicate_label   0.250   0->1 [0.025]
   splines   T   [T] F
   tenth_ticks   F   [F] T
   text_scale   1.000   [1.] (rel)
To change these options edit or create the plot option file
See: www.perplex.ethz.ch/perplex_plot_options.html

PostScript will be written to file: ex10.ps

Modify the default plot (y/n)?
N

Comparison between the P-T pseudosection calculated in Ex. 9 (XMgO=0.47) and the T-XMgO calculated at 3.5 kbar. **The sequence of mineral assemblages at increasing T should correspond in the two pseudosections.**

Ex. 11

Ex. 11 – DIRECT modelling of an anatectic METAPELITE (NKCFMASH system)

This exercise deals with the "DIRECT" modelling of a metapelite sample at supra-*solidus* conditions (i.e. melt-bearing). "Direct modelling" means that you know which is the protolith composition, <u>including its initial H₂O amount (which is generally not the case…).</u> In other worlds, we will consider a generic metapelite (with an average composition) and we will see what happens to this metapelite if it is heated enough to experience partial melting.

This exercise is based on the paper by White et al. (2001) [J. metam. Geol., 19, 139-153]. The P-T pseudosection is reported in their Fig. 4.

Bulk composition (mol%; SiO2 in excess):
Al2O3=30.66, FeO=23.74, MgO=12.47, CaO=0.97, Na2O=1.94, K2O=9.83, H2O=20.39
T=630-1000°C
P=0-12 kbar

(1) Definition of the problem (BUILD)

C:\PERPLEX\Perplex686>build

Perple_X version 6.8.6, source updated Jan 15, 2019.
Copyright (C) 1986-2019 James A D Connolly <www.perplex.ethz/copyright.html>.

NO is the default (blank) answer to all Y/N prompts

Enter a name for this project (the name will be used as the root for all output file names) [default = my_project]:
ex11

The problem definition file will be named: ex11.dat

Enter thermodynamic data file name [default = hp02ver.dat]:
hp62ver.dat

Enter the computational option file name [default = perplex_option.dat]:
See: www.perplex.ethz.ch/perplex_options.html
[enter]

Reading Perple_X options from: perplex_option.dat

The current data base components are:
 Na2O MgO Al2O3 SiO2 K2O CaO TiO2 MnO FeO NiO ZrO2 Cl2 O2 H2O CO2 CuO Cr2O3 S2 F2
Transform them (Y/N)?
n

Specify computational mode:

1 - Convex-Hull minimization

2 - Constrained minimization on a 2d grid [default]

3 - Constrained minimization on a 1d grid

4 - Output pseudocompound data

5 - 1-d Phase fractionation calculations

6 - 0-d Infiltration-reactionation-fractionation

7 - 2-d Phase fractionation (FRAC2D and TITRATE reactive transport models)

Use Convex-Hull minimization for Schreinemakers projections or phase diagrams with > 2 independent variables. Use constrained minimization for phase diagrams or phase diagram sections with < 3 independent variables.

2

Calculations with a saturated fluid (Y/N)?

Because specification of H_2O as a saturated phase component causes Perple_X to exclude any phases with the H_2O composition that are not named "H2O", **H2O should not be specified as a saturated fluid phase in calculations involving a hydrous silicate melt** if, as is commonly the case, the melt model involves a water end-member that is not named "H2O" (e.g. h2oL). **This means that, for calculations at supra-*solidus* conditions (e.g. melt-bearing systems), the user must consider H2O as a normal chemical component, and not as a saturated fluid phase.**

n

Calculations with saturated components (Y/N)?

y

warning ver015 if you select > 1 saturated component, then the order you enter the components determines the saturation heirarchy and may effect your results (see Connolly 1990).

Select < 6 saturated components from the set:

Na2O MgO Al2O3 SiO2 K2O CaO TiO2 MnO FeO NiO ZrO2 Cl2 O2 H2O CO2 CuO Cr2O3 S2   F2

Enter names, 1 per line, press <enter> to finish:

SiO2

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

n

Select thermodynamic components from the set:

 Na2O MgO Al2O3 K2O CaO TiO2 MnO FeO NiO ZrO2 Cl2 O2 H2O CO2 CuO Cr2O3 S2   F2

Enter names, 1 per line, press <enter> to finish:

Na2O

MgO

Al2O3

K2O

CaO

FeO

H2O

Because the thermodynamic data file identifies: H2O as special components, you will be prompted next for the EoS to be used for the corresponding composants and mixtures thereof. To override this behavior, e.g., to use a generic hybrid fluid EoS, delete the special_component section from the thermodynamic data file header.

Select fluid equation of state:
  0 - X(CO2) H2O-CO2 Modified Redlich-Kwong (MRK) DeSantis et al 74
  1 - X(CO2) H2O-CO2 HSMRK Kerrick & Jacobs 81
  2 - X(CO2) H2O-CO2 MRK hybrid-EoS*
  5 - X(CO2) H2O-CO2 CORK Holland & Powell 91, 98
  8 - f(O2/CO2) C-buffered COH MRK hybrid-EoS*
  10 - X(O) C-buffered COH MRK hybrid-EoS Connolly & Cesare 93*
  12 - X(O)-f(S2) C-buffered COHS MRK hybrid-EoS Connolly & Cesare 93*
  13 - X(H2) H2O-H2 MRK hybrid-EoS*
  14 - X(CO2) H2O-CO2 Pitzer & Sterner 94; Holland & Powell mixing 03
  15 - X(H2) H2O-H2 low T MRK hybrid-EoS*
  16 - X(O) H-O MRK hybrid-EoS*
  17 - X(O)-f(S2) H-O-S MRK hybrid-EoS*
  19 - X(O)-X(S) C-buffered COHS MRK hybrid-EoS Connolly & Cesare 93*
  20 - X(O)-X(C) COHS MRK hybrid-EoS Connolly & Cesare 93*
  24 - f(O2/CO2)-N/C C-buffered COHN MRK hybrid-EoS*
  25 - X(CO2)-X(NaCl) H2O-CO2-NaCl Aranovich et al 10
  26 - X(O) O-Si MRK Connolly 16
  27 - X(O)-X(C) C-O-H MRK hybrid-EoS*
*Hybrid EoS use the following pure species EoS, to change these associations modify the hybrid_EoS keywords in the perplex_option file:
    H2O - PSEoS Pitzer & Sterner 1994
    CO2 - PSEoS Pitzer & Sterner 1994
    CH4 - HSMRK Kerrick & Jacobs 1981
5

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

Select x-axis variable:
   1 - P(bar)
   2 - T(K)
   3 - Composition X_C1* (user defined)
*X_C1 can not be selected as the y-axis variable
2

Enter minimum and maximum values, respectively, for: T(K)
903
1273

Enter minimum and maximum values, respectively, for: P(bar)
0.1
12000

For gridded minimization, grid resolution is determined by the number of levels (grid_levels) and the resolution at the lowest level in the X- and Y-directions (x_nodes and y_nodes) these parameters are currently set for the exploratory and autorefi ne cycles as follows:

stage	grid_levels	xnodes	ynodes	effective resolution
exploratory	1	60	60	60 x 60 nodes
auto-refine	4	60	60	473 x 473 nodes

To change these options edit or create the file perplex_option.dat
See: www.perplex.ethz.ch/perplex_options.html#grid_parameters

All thermodynamic components must be constrained,
specify saturated components also (Y/N)?
n

Specify component amounts by mass (Y/N)?
n

The amounts you enter next need not be normalized; regardless of units, they define the molar amount of the system

Enter the molar amounts of the components:
 Na2O MgO   Al2O3 K2O   CaO   FeO   H2O
for the bulk composition of interest:
1.94
12.74
30.66
9.83
0.97
23.74
22.39

Output a print file (Y/N)?
y

warning ver051 cannot make hmjL because of missing data or an invalid definition in the thermodynamic data file.
…

Exclude pure and/or endmember phases (Y/N)?
y
Do you want to be prompted for phases (Y/N)?
n
Enter names, 1 per line, press <enter> to finish:
ab
mic

Include solution models (Y/N)?
y
Enter the solution model file name [default = solution_model.dat]:
[enter]

warning ver025 0 endmembers for FeS_liq   The solution will not be considered.

Select models from the following list, enter 1 per line, press <enter> to finish
clinopyroxene models: Cpx(H)   Augite(G) Cpx(JH) Cpx(l)   Cpx(h) Cpx(stx) Cpx(stx7) Omph(HP) Cpx(HP)
                        Cpx(m)   Cpx(stx8) Omph(GHP)

clinoamphibole models: cAmph(G)   Cumm   Gl   Tr   Act(M)   cAmph(DP) cAmph(G)_I GlTrTsMr
                          Ca-Amph(D) Na-Amph(D)   GlTrTsPg   Amph(DHP) Amph(DPW)

liquid models: melt(H)   melt(G)   Melt(JH)   melt(W)   melt(HP)

chlorite models: Chl(W)   Chl(HP)   Chl(LWV)

olivine models: O(JH)   O(SG)   O(HP)   O(HPK)   O(stx)   O(stx7)   Ol(m)   O(stx8)

spinel models: Sp(JH)   GaHcSp   Sp(JR)   Sp(GS)   Sp(HP)   Sp(stx)   CrSp   Sp(stx7)   Sp(WPC)   Sp(stx8)

binary-feldspar models: Pl(JH)   Pl(h)   Kf   San   San(TH)   Pl(stx8)

garnet models: Grt(JH)   Gt(W)   CrGt   Gt(MPF)   Gt(B)   Gt(GCT)   Gt(HP)   Gt(EWHP)   Gt(WPH)   Gt(stx)
                      Gt(stx8)   Gt(WPPH)   ZrGt(KP)   Maj

orthopyroxene models: Opx(JH)   Opx(W)   Opx(HP)   CrOpx(HP) Opx(stx)   Opx(stx8)

white-mica models: Mica(W)   Pheng(HP) MaPa   Mica(CF)   Mica(CHA1)   Mica(CHA) Mica+(CHA) Mica(M)
                        Mica(SGH)

chloritoid models: Ctd(W)   Ctd(HP)   Ctd(SGH)

staurolite models: St(W)   St(HP)

biotite models: Bi(W)   Bio(TCC)   Bio(WPH)   Bio(HP)

cordierite models: Crd(W)   hCrd

sapphirine models: Sa(WP)   Sapp(TP)   Sapp(HP)   Sapp(KWP)

pumpellyite models: Pu

carpholite models: Carp   Carp(M)   Carp(SGH)

sudoite models: Sud(Livi) Sud   Sud(M)

orthoamphibole models: Anth   oAmph(DP) o-Amph

ternary-feldspar models: feldspar   feldspar_B Pl(I1,HP) Fsp(C1)

stilpnomelane models: Stlp

alphabet-phase models: A-phase

clinohumite models: Chum

brucite models: B

aqueous_electrolyte model WADDAH

wadleysite models: Wad

ringwoodite models: Ring   Ring(H)

wuestite models: Wus

ilmenite models: Aki

perovskite models: Pv

High pressure garnet mode Gt(H)

ferropericlase models: Fper(H)

MgSi Perovskite models: Mpv(H)

CaSi Perovskite models: Cpv(H)

Corundum models: Cor(H)

Akimotoite models: Aki(H)

wadsleyite models: Wad(H)

HP_clinopyroxene models: Hpx(H)

talc models: T

serpentine models: Atg(PN)

For details on these models see:www.perplex.ethz.ch/perplex_solution_model_glossary.html or read the commentary in the solution model file.

Bi(W)

Mica(W)

Gt(W)

St(W)

Crd(W)

Opx(W)

feldspar
melt(W)

Enter calculation title:
Ex11

(2) Doing the calculation (VERTEX)

Run VERTEX to make the calculation:

C:\PERPLEX\Perplex686>vertex

Perple_X version 6.8.6, source updated Jan 24, 2019.
Copyright (C) 1986-2019 James A D Connolly <www.perplex.ethz/copyright.html>.

Enter the project name (the name assigned in BUILD) [default = my_project]:
Ex11
…
warning ver114 the following endmembers are missing for Gt(W)
  spss   fmn_i   fkho_i   kho1   andr_i
warning ver050 reformulating prismatic solution: Gt(W)   because of missing endmembers.
(reformulation can be controlled explicitly by excluding additional endmembers).
    150 pseudocompounds generated for: Gt(W)

error ver180 too many pseudocompounds 16000000 generated subdividing site 1 of solution: melt(W)
this error can usually be eliminated by one of the following actions (best listed first):
  - increase the 1st value of the initial_resolution keyword in in perplex_option.dat
  - restrict the subdivision range for the solution
  - if non-linear subdivision is specified for the solution then increase the resolution parameters or change to linear subdivision
  - increase parameter k13 and recompile

Press Enter to quit...

The calculation ends abruptly with an error message explaining that VERTEX has generated **TOO MANY PSEUDOCOMPOUNDS** for the solution model "melt(W)". There are four suggestions to overcome this problem (i.e. to decrease the number of generated pseudocompounds): suggestion (1) implies to make changes in the perplex_option file, suggestions (2) and (3) imply to make changes in the solution_model file, whereas suggestion (4) is out of our reach (it means that it is necessary to recompile VERTEX). **I suggest to follow suggestion (1), i.e. to modify the initial_resolution values in the perplex_option.dat file.**
The default values of the initial_resolution keyword are currently set as: 1/16 (exploratory stage) and 1/48 (auto-refine stage).
The new suggested values are: **1/10 (exploratory stage) and 1/16 (auto-refine stage)**.

initial_resolution   1/10 1/16 | [1/16] >0, <1

I suggest to rename BOTH the perplex_option file (e.g. perplex_option_ex11.dat) AND the input file (e.g. ex11_2); remember to change the name of the perplex_option file in the input file.

C:\PERPLEX\Perplex686>vertex

Perple_X version 6.8.6, source updated Jan 24, 2019.
Copyright (C) 1986-2019 James A D Connolly <www.perplex.ethz/copyright.html>.

Enter the project name (the name assigned in BUILD) [default = my_project]:
Ex11_2

…

(3) Plotting the calculated phase diagram (PSSECT)

Run PSSECT to plot the calculated pseudosection:

C:\PERPLEX\Perplex686>pssect

Perple_X version 6.8.6, source updated Jan 24, 2019.
Copyright (C) 1986-2019 James A D Connolly <www.perplex.ethz/copyright.html>.

Enter the project name (the name assigned in BUILD) [default = my_project]:
Ex11_2

Reading Perple_X options from: perplex_option.dat

Perple_X plot options are currently set as:
```
  Keyword:          Value:     Permitted values [default]:
  axis_label_scale    1.20       [1.2] (rel)
  bounding_box :
                0     [0] x-min (pts)
                0     [0] y-min (pts)
              800     [800] x-length (pts)
              800     [800] y-length (pts)
  field_fill        T       [T] F
  field_label       T       [T] F
  field_label_scale   0.75     [0.72] (rel)
  font            Helvetica
  grid            F       [F] T
  half_ticks        T       [T] F
  line_width        1.00     0-99 [1.] (pts)
  picture_transformation :
              0.180    [0.18] x-scale (rel)
              0.180    [0.18] y-scale (rel)
              130.    [0.18] x-translation (pts)
              220.    [0.18] y-translation (pts)
              0.00    [0.0]  rotation (deg)
  plot_aspect_ratio   1.000    [1.0] x_axis_length/y_axis_length
  replicate_label     0.250     0->1 [0.025]
  splines          T       [T] F
  tenth_ticks        F        [F] T
```

```
     text_scale        1.000     [1.] (rel)
```
To change these options edit or create the plot option file
See: www.perplex.ethz.ch/perplex_plot_options.html

PostScript will be written to file: ex11.ps

Modify the default plot (y/n)?
n

warning ver099 the section contains phase fields of variance > 6 these will be drawn with pattern fills
that may look strange. Suppress phase field fills for fields with variance > 6 (y/n)?
n
There are 10 fields for: Opx Bio Crd Fsp Fsp H2O
There are 14 fields for: Gt Melt Mica Bio Fsp H2O
There are   4 fields for: Mica Bio Fsp Fsp sill H2O
There are   3 fields for: Gt Melt Mica Bio Fsp ky
There are   2 fields for: Mica St Bio Fsp sill H2O
There are   2 fields for: Gt Mica St Bio Fsp sill H2O

(4) Calculating ISOMODES (WERAMI)

This section explains how to calculate the **variation in the modal amounts** of each phase (vol%) for the modelled pseudosection. There are also suggestions for calculating **isomodes for 2 immiscible phases (i.e. Pl and Kfs) of the same solution (i.e. feldspar) coexisting in one or more fields**.

Run WERAMI to calculate the ISOMODES of each phase.

C:\PERPLEX\Perplex686>werami

Perple_X version 6.8.6, source updated Jan 24, 2019.
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Enter the project name (the name assigned in BUILD) [default = my_project]:
ex11_2

Reading Perple_X options from: perplex_option.dat
Writing Perple_X option summary to file: not requested

Perple_X version 6.8.6, source updated Jan 24, 2019.
Copyright (C) 1986-2019 James A D Connolly <www.perplex.ethz/copyright.html>.

Perple_X computational option settings for WERAMI:

Keyword: Value: Permitted values [default]:

Input/Output options:

```
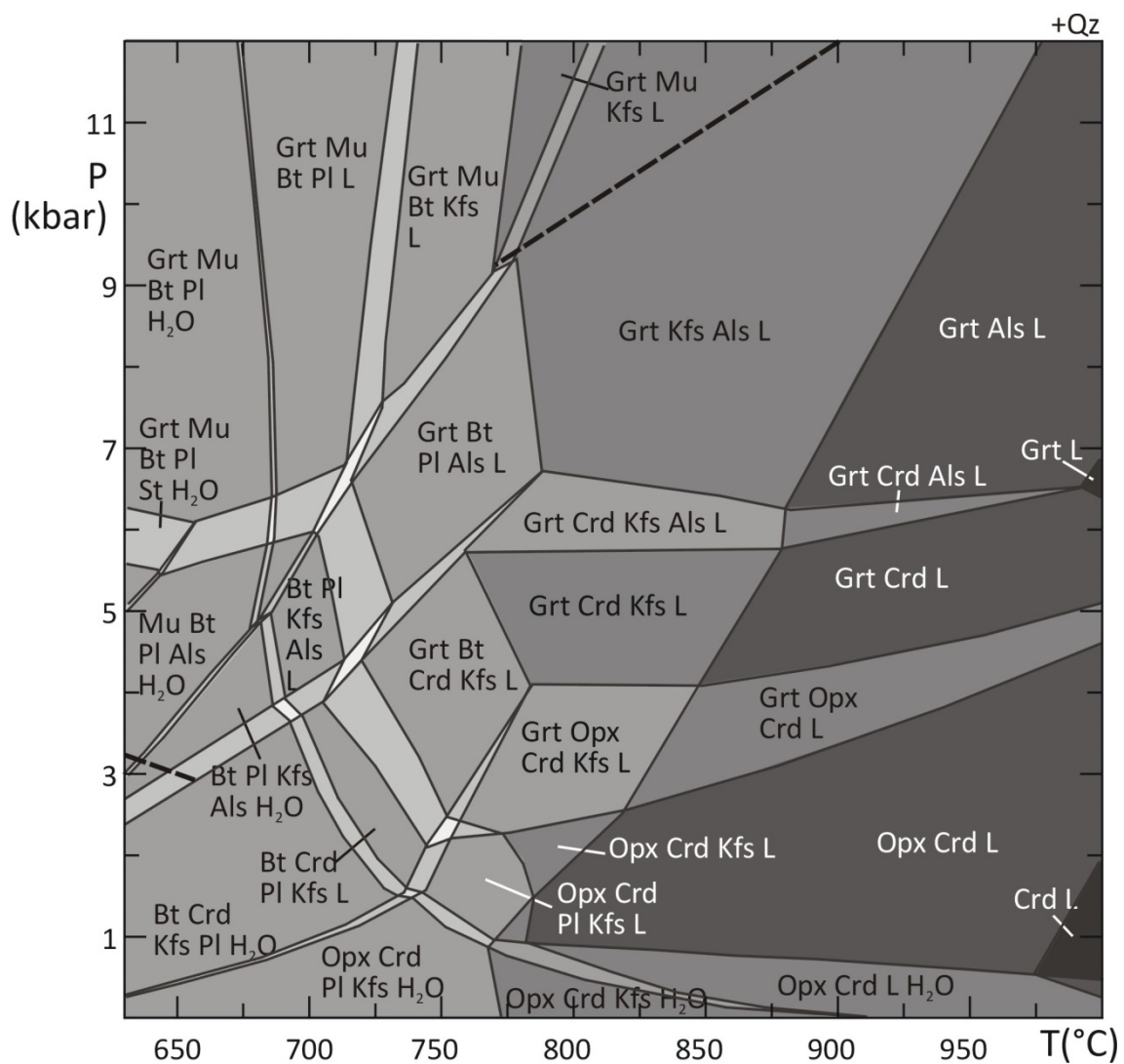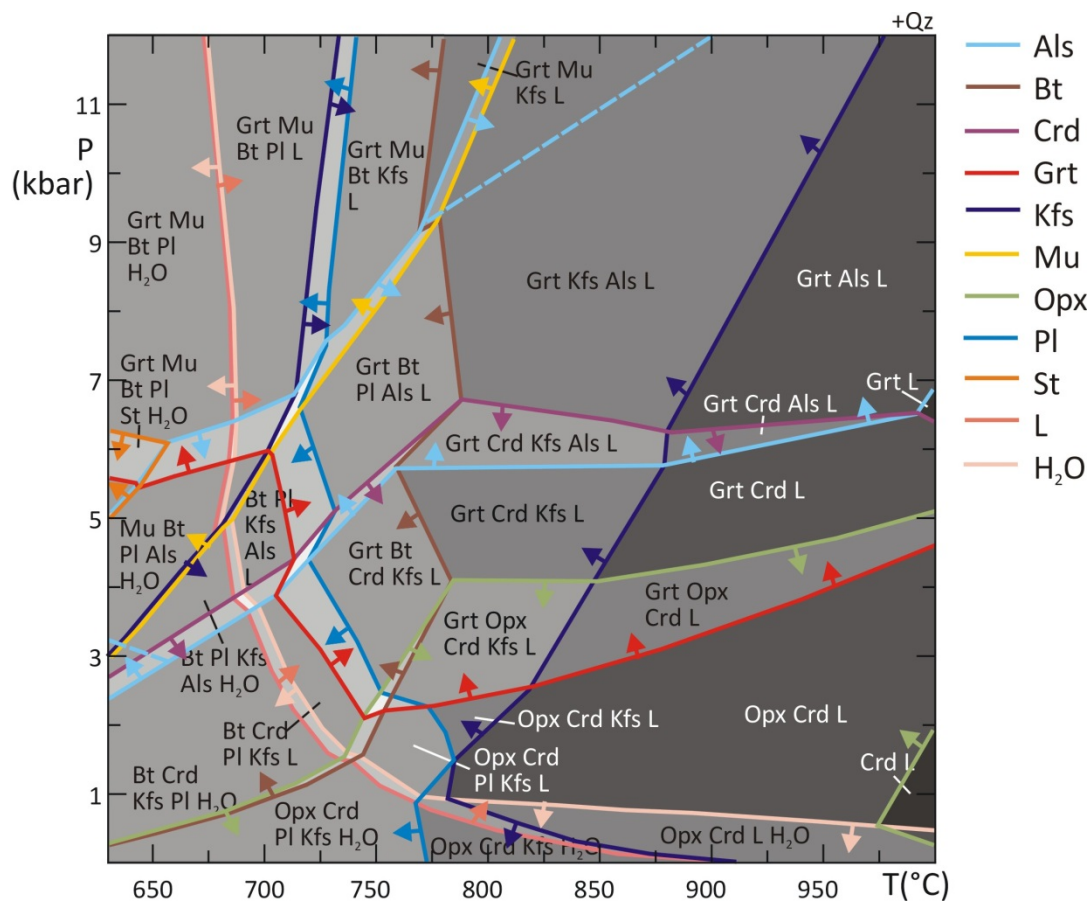aqueous_output       T        [F] T
aqeuous_species      20       [20] 0-100
aq_solvent_composition y      [y] m: y => mol fraction, m => molality
aq_solute_composition  m      y [m]: y => mol fraction, m => molality
spreadsheet          T        [F] T
logarithmic_p        F        [F] T
bad_number           NaN      [NaN]
composition_constant F        [F] T
composition_phase    mol      [mol] wt
composition_system   wt       [wt] mol
proportions          vol      [vol] wt mol
absolute             F        [F] T
cumulative           F        [F] T
fancy_cumulative_modes F      [F] T
interpolation        on       [on] off
melt_is_fluid        F        [F] T
solution_names       abb      [model] abbreviation full
species_output       T        [T] F
species_Gibbs_energies F      [F] T
seismic_output       som      [some] none all
pause_on_error       T        [T] F
poisson_test         F        [F] T
interim_results      aut      [auto] off manual
sample_on_grid       F        [T] F
auto_exclude         T        [T] F
```

Information file output options:

```
option_list_files    F        [F] T; echo computational options
```

Thermodynamic options:

```
approx_alpha         T        [T] F
Anderson-Gruneisen   F        [F] T
hybrid_EoS_H2O       4        [4] 0-2, 4-7
hybrid_EoS_CO2       4        [4] 0-4, 7
hybrid_EoS_CH4       0        [0] 0-1, 7
fd_expansion_factor  2.0      >0 [2.]
finite_difference_p  0.1D+05  >0 [1d4]; fraction = 0.1D-02  [1d-2]
```

Seismic velocity options:

```
bounds               VRH      [VRH] HS
vrh/hs_weighting     0.5      [0.5] 0->1
explicit_bulk_modulus T       [F] T
poisson_ratio        on       [on] all off; Poisson ratio = 0.35
```

To change these options see: www.perplex.ethz.ch/perplex_options.html

Select operational mode:

    1 - properties at specified conditions

    2 - properties on a 2d grid

    3 - properties along a 1d path

4 - as in 3, but input from file
    0 - EXIT
2

Select a property [enter 0 to finish]:
   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 - Composition (Mol, Mass, or Wt%) of the system
   7 - Mode (Vol, Mol, or Wt proportion) of a phase
   8 - Composition (Mol, Mass, or Wt%) of a solution phase
   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-system)
  21 - Poisson ratio
  22 - Molar Volume (J/bar)
  23 - Dependent potentials (J/mol, bar, K)
  24 - Assemblage Index
  25 - Modes of all phases
  26 - Sound velocity T derivative (km/s/K)
  27 - P-wave velocity T derivative (km/s/K)
  28 - S-wave velocity T derivative (km/s/K)
  29 - Adiabatic bulk modulus T derivative (bar/K)
  30 - Shear modulus T derivative (bar/K)
  31 - Sound velocity P derivative (km/s/bar)
  32 - P-wave velocity P derivative (km/s/bar)
  33 - S-wave velocity P derivative (km/s/bar)
  34 - Adiabatic bulk modulus P derivative (unitless)
  35 - Shear modulus P derivative (unitless)
  36 - All phase &/or system properties
  37 - Absolute amount (Vol, Mol, or Wt) of a phase
  38 - Multiple property output
  39 - Heat capacity ratio (Cp/Cv)
  40 - Lagged or back-calculated aqueous solute chemistry
7

Enter solution or compound (left justified):
melt(W)
Include fluid in computation of aggregate (or modal) properties (y/n)?
You should answer N if you want to calculate the modal amounts of solid phases.

n

Fractions are Wt, Vol, or Mol depending on the perplex_option.dat proportions keyword.

Select a property [enter 0 to finish]:

7

Enter solution or compound (left justified):

Mica(W)

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

n

Fractions are Wt, Vol, or Mol depending on the perplex_option.dat proportions keyword.

Select a property [enter 0 to finish]:

7

Enter solution or compound (left justified):

Bi(W)

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

n

Fractions are Wt, Vol, or Mol depending on the perplex_option.dat proportions keyword.

Select a property [enter 0 to finish]:

7

Enter solution or compound (left justified):

feldspar

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

n

Fractions are Wt, Vol, or Mol depending on the perplex_option.dat proportions keyword.

Select a property [enter 0 to finish]:

7

Enter solution or compound (left justified):

Gt(W)

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

n

Fractions are Wt, Vol, or Mol depending on the perplex_option.dat proportions keyword.

Select a property [enter 0 to finish]:

7

Enter solution or compound (left justified):

Crd(W)

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

n

Fractions are Wt, Vol, or Mol depending on the perplex_option.dat proportions keyword.

Select a property [enter 0 to finish]:

7

Enter solution or compound (left justified):

Opx(W)

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

n

Fractions are Wt, Vol, or Mol depending on the perplex_option.dat proportions keyword.

Select a property [enter 0 to finish]:

7

Enter solution or compound (left justified):

ky

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

n

Fractions are Wt, Vol, or Mol depending on the perplex_option.dat proportions keyword.

Select a property [enter 0 to finish]:

7

Enter solution or compound (left justified):

sill

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

n

Fractions are Wt, Vol, or Mol depending on the perplex_option.dat proportions keyword.

Select a property [enter 0 to finish]:

7

Enter solution or compound (left justified):

and

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

n

Fractions are Wt, Vol, or Mol depending on the perplex_option.dat proportions keyword.

Select a property [enter 0 to finish]:

0

Change default variable range (y/n)?

n

Select the grid resolution (to use an arbitrary grid set sample_on_grid to F):
   1 -   60 x   60 nodes
   2 - 119 x 119 nodes
   3 - 237 x 237 nodes
   4 - 473 x 473 nodes [default]

4

...

...

2 immiscible phases of feldspar coexist with the following molar compositions:

H2O	MgO	Al2O3	K2O	CaO	FeO	Na2O	SiO2
0.000	0.000	0.505	0.422	0.010	0.000	0.073	2.990
0.000	0.000	0.789	0.009	0.577	0.000	0.202	2.423

Identify the phase of interest by:

1 - the maximum value of a composition [default].

2 - the minimum value of a composition.

3 - the range of one or more compositions.

4 - a combination of the above.

5 - average the compositions of immiscible phases.

Kfs and Pl have been modelled using the same solid solution model ("feldspar"); therefore, in the modelled pseudosection, you have fields in which two feldspars coexist. For those fields where there are two stable feldspars, you should specify what do you want to calculate (i.e. isomodes for Kfs or for Pl?).

You should choose one of the above criteria: for example, if you want to calculate the isomodes for plagioclase, you can specify that the phase of interest should be identified basing on the maximum anorthite content (and, conversely, if you want to calculate the isomodes for K-feldspar, it should be identified basing on the maximum sanidine content, or the minimum anorthite content).

1

The following prompts define the composition C[1] to be used to identify the phase of interest.

NOTE: discriminatory criteria are only applied when immiscible phases coexist. If only one phase of a solution is stable, then data for this phase is output regardless of whether the phase meets the criteria specified here.

Read carefully this note.

Define the composition in terms of the species/endmembers of feldspar (y/n)?

Answer no to define a composition in terms of the systems components. Units (mass or molar) are controlled by the composition keyword in perplex_option.dat.

y

Compositions are defined as a ratio of the form:

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

y(j)   = mole fraction of species j

w(j)   = weighting factor of species j (usually 1)

How many components in the numerator of the composition (<13)?

1

Enter species indices and weighting factors for the numerator:

1 - abh

2 - an

3 - san

2

1

How many species in the denominator of the composition (<12)?

Enter zero to use the numerator as a composition.

0

The compositional variable is: 1.0 an

Change it (y/n)?

n

Remember that you are calculating the isomodes of plagioclase in those fields where two feldspar coexist. In the fields where you have only one feldspar, the calculated isomodes refer to either Pl or Kfs, depending on which one is stable.

In order to calculate the isomodes of K-feldspar in the fields where two feldspar coexists, you should run again WERAMI, asking for Kfs isomodes.

…

Output has been written to the 2d tab format file: ex10_1.tab

2d tab format files can be processed with:
    PSTABLE - a Perple_X plotting program
    PERPLE_X_PLOT - a MATLAB plotting script
    PYWERAMI - petrol.natur.cuni.cz/~ondro/pywerami:home
    spread-sheet programs, e.g., EXCEL
for details on tab format refer to:
    perplex.ethz.ch/faq/perple_x_tab_file_format.txt

Select operational mode:
    1 - properties at specified conditions
    2 - properties on a 2d grid
    3 - properties along a 1d path
    4 - as in 3, but input from file
    0 - EXIT
0

At the end, you have a new file (ex10_1.tab) in the Perple_X folder.

Run again WERAMI to calculate isomodes for K-feldspar (ex10_2.tab).

NB: If you have doubts on which feldspar is stable in each field assemblage, you can run WERAMI, option 1. This option allows to calculate all the properties of the system (including phase compositions) at specified P-T conditions.

For example at **973 K (700°C), 8 kbar**:

Stable phases at:

$$T(K) = 973.000$$
$$P(bar) = 8000.00$$

Phase Compositions (molar proportions):

	wt %	vol %	mol %	mol	H2O	MgO	Al2O3	K2O	CaO	FeO	Na2O	SiO2
Gt	19.11	14.03	15.33	4.80	0.00000	0.54157	1.00000	0.00000	0.08591	2.37251	0.00000	3.000
Melt	2.75	3.91	10.27	3.21	0.65039	0.00118	0.13549	0.04210	0.00404	0.00378	0.08089	1.129
Mica	41.23	44.24	39.79	12.5	1.00000	0.05226	1.40016	0.45752	0.00360	0.04938	0.04068	3.098
Bio	30.30	30.19	25.06	7.84	1.00000	1.20938	0.79539	0.50000	0.00000	1.49523	0.00000	2.704
Fsp	**6.61**	**7.64**	**9.57**	**2.99**	**0.00000**	**0.00000**	**0.58347**	**0.02474**	**0.16694**	**0.00000**	**0.39178**	**2.833**

Phase speciation (molar proportions):

Gt   alm: 0.79084, py: 0.18052, gr: 0.02864

Melt   fo8L: 0.00029, fa8L: 0.00094, abL: 0.16179, sil8L: 0.00528, anL: 0.00404, kspL: 0.08421, q8L: 0.09305
         h2oL: 0.65039

Mica   mu: 0.81339, pa: 0.08137, ma1_dqf: 0.00360, cel: 0.05226, fcel: 0.04938

Bio   east: 0.29539, ann: 0.51700, phl: 0.24337, obi: -0.05576

Fsp   abh: 0.78357, an: 0.16694, san: 0.04949

Ex. 12

Ex. 12 – INDIRECT modelling of an anatectic METAPELITE

In Ex. 11 we have considered a model metapelite, and we have supposed to know the protolith bulk composition (including its initial H_2O amount). However, **in most cases, we have to deal with natural samples, of which we do not know the whole history.** Furthermore, **a number of evidence are consistent with most migmatites and granulites having lost some to virtually all of their melt during metamorphism.**

This exercise aims at modelling a REAL SAMPLE OF ANATECTIC METAPELITE.

What do we know?	**What we do not know?**
• The observed mineral assemblage	• The bulk composition of the protolith (if a certain amount of melt was lost during the prograde evolution)
• The measured mineral compositions	
• The measured bulk composition (which often does not coincide with the composition of the protolith!)	• The amount of melt that was lost
	• The number of melt loss events
	• The P-T conditions at which melt was lost

STRATEGY

The problem can be divided in two parts:

(A) If a certain amount of melt was lost during the prograde evolution, the measured bulk composition of the sample represents the FINAL rock composition, after the loss of that melt. Therefore, the pseudosection calculated using the **MEASURED bulk composition** allows to constrain the **P-T evolution from peak conditions to final melt crystallization (i.e. retrograde evolution)**, but may not be valid for the prograde evolution of the rock.

(B) An **APPROXIMATE PROTOLITH COMPOSITION** can be calculated by REINTEGRATING melt into the measured rock composition. The pseudosection calculated using the **MELT-REINTEGRATED bulk composition** allows the exploration of the extended supra-*solidus* domain and the assessment of an **APPROXIMATE prograde evolution**.

This exercise is based on the paper by Groppo et al. (2012) [J. Petrol., 53, 1057-1088]. The P-T pseudosection is reported in their Fig. 10a.

MEASURED BULK COMPOSITION

Bulk composition may be obtained using conventional methods (e.g. XRF, ICP-MS), **BUT** we need a precise estimate of the H_2O amount in the bulk. A PRECISE ESTIMATE OF THE H_2O CONTENT IN THE BULK is, in fact, crucial because it controls the position of the *solidus* and the amount of melt that can be produced from the source rock as a function of P-T. **Conventional methods do not provide such an accurate estimate of H_2O content (do not thrust the LOI value!)**.

My suggested method is to combine the mineral proportions obtained from the modal estimate of a compositional map of the whole thin section with the mineral chemistry acquired at the microprobe. This method allows a precise estimate of the modal percentage of hydrous minerals (e.g. biotite, cordierite) in the rock, which is required to derive the H_2O content in the bulk.

Micro-XRF maps

Modal amounts of minerals

vol%	07-35
Qtz	51.7
Kfs	14.3
Sil	5.1
Bt	9.2
Grt (low Ca)	2.9
Grt (high Ca)	1.9
Pl	14.7
Rt	0.1
	100.0

Qtz
Kfs
Pl
Bt
low-Ca Grt
high-Ca Grt
Ky/Sil
Rt

1 cm

Bulk composition

	07-35	
	mol%	wt%
SiO_2	79.45	74.58
TiO_2	0.57	0.71
Al_2O_3	8.6	13.7
FeO	3.49	3.92
MnO	0.06	0.07
MgO	2.18	1.37
CaO	1.11	0.97
Na_2O	1.5	1.45
K_2O	2	2.94
H_2O	1.04	0.29
	100.0	100.0

(1) Definition of the problem (BUILD)

Bulk composition (mol%):

SiO2=79.45; TiO2: 0.57; Al2O3=8.6, FeO=3.49, MgO=2.18, CaO=1.11, Na2O=1.5, K2O=2.00, H2O=1.04

T=700-900°C

P=3-15 kbar

Because the problem is similar to that of Ex. 11, we can try to skip the BUILD session and to directly edit the input file, starting from that of Ex. 11_2 (Use the perplex_option_ex11.dat file created for Ex11).

NB: SiO2 is not considered in excess; add TiO2 and MnO in the list of thermodynamic components; change the P-T range of interest; exclude Chl(W), St(W) and Ctd(W) (these are surely not stable at T > 700°C).

(2) Doing the calculation (VERTEX)

Run vertex to make the calculation:

C:\PERPLEX\Perplex686>vertex

Perple_X version 6.8.6, source updated Jan 24, 2019.
Copyright (C) 1986-2019 James A D Connolly <www.perplex.ethz/copyright.html>.

Enter the project name (the name assigned in BUILD) [default = my_project]:
Ex12

…

(3) Plotting the calculated phase diagram (PSSECT)

Run PSSECT to plot the calculated pseudosection:

C:\PERPLEX\Perplex686>pssect

Perple_X version 6.8.6, source updated Jan 24, 2019.
Copyright (C) 1986-2019 James A D Connolly <www.perplex.ethz/copyright.html>.

Enter the project name (the name assigned in BUILD) [default = my_project]:
Ex12

...

Figure labels (pseudosection, P(bar) vs T(K)):
- Gt Mica Fsp Fsp ky q ru
- Gt Melt Mica Fsp Fsp ky q ru
- Gt Melt Fsp Fsp ky q ru
- Gt Mica Bio Fsp Fsp ky q ru
- Gt Melt Mica Bio Fsp Fsp ky q ru
- Gt Melt Bio Fsp Fsp ky q ru
- Gt Bio Fsp Fsp ky q ru
- Gt Melt Fsp Fsp sill q ru
- Gt Bio Fsp Fsp sill q ru
- Gt Melt Bio Fsp Fsp sill q ru
- Gt Bio Fsp Fsp sill q ru ilm
- Gt Melt Bio Fsp Fsp sill q ru
- Gt Melt Bio Crd Fsp Fsp sill q ru
- Gt Melt Bio Fsp Fsp sill
- Gt Melt Crd Fsp Fsp sill q ru
- Gt Melt Crd Fsp Fsp sill q ru ilm
- Gt Bio Fsp Fsp sill q ilm
- Gt Melt Bio Crd Fsp Fsp sill q ilm
- Gt Melt Crd Fsp Fsp sill q ilm
- Gt Bio Crd Fsp Fsp sill q ilm
- Gt Crd Fsp Fsp q ilm
- Gt Melt Crd Fsp Fsp q ilm
- Gt Bio Crd Fsp Fsp q ilm
- Gt Melt Bio Crd Fsp Fsp q ilm
- Gt Melt Opk Crd Fsp Fsp q ilm

Peak P-T conditions can be derived by:

(a) the stability field of the peak assemblage (Grt + Bt + Kfs + Pl + Sil + Qtz + Rt + L);

(b) the modelled vs. observed garnet composition (see details in Groppo et al., 2012)

P-T conditions of final melt crystallization are given by:

(a) the intersection between the MODELLED ISOMODES of each phase and the *solidus*, that should correspond to the MEASURED mineral modes.

Comparison with Fig. 10a in Groppo et al. (2012). Note that, although minor changes occur in the topology of the pseudosection due to the different thermodynamic databases and solid solution models used, the final results are very similar.

Option 1 of WERAMI allows to quickly check if the modelled mineral modes at the *solidus* (i.e. at P-T conditions estimated for the final melt crystallization: 770°C, 6 kbar) are comparable (within the error) with the observed mineral modes.

Werami, option 1
Stable phases at:

    T(K)   = 1053.00
    P(bar) = 6000.00

Phase Compositions (molar proportions):

	wt %	vol %	mol %	mol	H2O	TiO2	Na2O	MgO	Al2O3	K2O	CaO	FeO
Gt	5.26	3.51	1.12	0.710	0.00000	0.00000	0.00000	0.73281	1.00000	0.00000	0.07031	2.19688
Bio	9.42	8.46	2.05	1.31	0.79661	0.20339	0.00000	1.27102	0.78112	0.50000	0.00000	1.24447
Fsp	14.26	15.20	5.22	3.32	0.00000	0.00000	0.12240	0.00000	0.51270	0.36491	0.02539	0.00000
Fsp	14.37	14.87	5.39	3.43	0.00000	0.00000	0.31870	0.00000	0.64223	0.03906	0.28447	0.00000
sill	7.50	6.30	4.66	2.96	0.00000	0.00000	0.00000	0.00000	1.00000	0.00000	0.00000	0.00000
q	48.47	51.23	81.09	51.6	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
ilm	0.72	0.42	0.48	0.304	0.00000	1.00000	0.00000	0.00000	0.00000	0.00000	0.00000	1.00000

Mineral modes		
770°C, 6 kbar		
	observed	modelled
Qtz	51.7	51.2
Kfs	14.3	15.2
Sil	5.1	6.3
Bt	9.2	8.5
Grt	4.8	3.5
Pl	14.7	14.9

Ex. 12.2 – PROGRADE P-T EVOLUTION and MELT RE-INTEGRATION

This exercise is based on the paper by Groppo et al. (2012) [J. Petrol., 53, 1057-1088]. The P-T pseudosection is reported in their Fig. 10b.

In natural systems, it is not possible to know exactly the total amount and composition of missing melt and the number of episodes of melt loss, therefore the EXACT missing melt cannot be added back to reconstruct the real sub-*solidus* protolith composition. As a consequence, **the prograde portion of the P-T evolution of anatectic rocks is generally less well constrained than the retrograde one.**

An APPROXIMATE protolith composition can be calculated by reintegrating melt into the measured rock composition. It has been demonstrated that the simple case of **a single event of melt loss (occurred at peak T conditions)** is a defensible end-member case.

(i) How much melt should be re-integrated?
An amount of melt sufficient to model a H_2O-saturated *solidus* in the pressure range of interest.
This melt-reintegrated composition likely approximates that of a protolith containing the maximum possible amount of mica before melting.

How to calculate the amount of melt to be reintegrated
Use a **trial and error method**.
- start from the measured bulk composition and add a small amount of melt (e.g. 0.05 mol%); calculate a new pseudosection with the reintegrated bulk composition (better if you extend the T range down to 650°C); check if the modelled *solidus* is still dry or wet.
- repeat this process until a H_2O-saturated (wet) *solidus* is modelled in the P-range of interest.

(ii) Of which composition?
The composition of reintegrated melt can be calculated at peak-T conditions.

How to estimate the melt composition to be reintegrated
Run WERAMI, option 1, at peak P-T conditions. The melt composition is expressed in molar proportions of oxides (see below).

Run Werami, option 1 to estimate the melt composition at peak T conditions (780°C, 8.0 kbar)

Stable phases at:
T(K)   = 1053.00
P(bar) = 8000.00

Phase Compositions (molar proportions):

	wt %	vol %	mol %	mol	H2O	TiO2	Na2O	MgO	Al2O3	K2O	CaO	FeO	SiO2
Gt	7.44	5.00	1.59	1.01	0.00000	0.00000	0.00000	0.73672	1.00000	0.00000	0.10156	2.16172	3.00000
Melt	**0.60**	**0.74**	**0.48**	**0.301**	**0.55196**	**0.00000**	**0.07194**	**0.00218**	**0.17966**	**0.07513**	**0.01112**	**0.00641**	**1.43928**
Bio	7.86	7.09	1.73	1.09	0.79922	0.20078	0.00000	1.31508	0.78307	0.50000	0.00000	1.20107	2.71693
Fsp	14.96	15.97	5.52	3.49	0.00000	0.00000	0.11589	0.00000	0.51237	0.37174	0.02474	0.00000	2.97526
Fsp	13.97	14.49	5.28	3.34	0.00000	0.00000	0.32202	0.00000	0.63761	0.04036	0.27522	0.00000	2.72478
sill	7.02	5.91	4.39	2.77	0.00000	0.00000	0.00000	0.00000	1.00000	0.00000	0.00000	0.00000	1.00000
q	47.71	50.52	80.45	50.8	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	1.00000
ru	0.44	0.28	0.55	0.350	0.00000	1.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000

Calculate the re-integrated bulk compositions adding small amounts of melt to the measured bulk composition.

	melt composition (780°C, 7.6 kbar)		BC**	Melt reintegrated bulk compositions							
				+ 0.05 mol%		+ 0.10 mol%		+ 0.15 mol%		+ 0.20 mol%	
	mol*	mol%	mol%		mol%		mol%		mol%		mol%
SiO2	1.4393	61.57	79.45	82.5	78.60	85.6	77.82	88.7	77.12	91.8	76.47
TiO2	0.0000	0.00	0.57	0.6	0.54	0.6	0.52	0.6	0.50	0.6	0.48
Al2O3	0.1797	7.69	8.60	9.0	8.56	9.4	8.52	9.8	8.48	10.1	8.45
FeO	0.0064	0.27	3.49	3.5	3.34	3.5	3.20	3.5	3.07	3.5	2.95
MnO	0.0000	0.00	0.06	0.1	0.06	0.1	0.05	0.1	0.05	0.1	0.05
MgO	0.0022	0.09	2.18	2.2	2.08	2.2	1.99	2.2	1.91	2.2	1.83
CaO	0.0111	0.48	1.11	1.1	1.08	1.2	1.05	1.2	1.03	1.2	1.00
Na2O	0.0719	3.08	1.50	1.7	1.58	1.8	1.64	2.0	1.71	2.1	1.76
K2O	0.0751	3.21	2.00	2.2	2.06	2.3	2.11	2.5	2.16	2.6	2.20
H2O	0.5520	23.61	1.04	2.2	2.11	3.4	3.09	4.6	3.98	5.8	4.80
Total	2.3377	100.00	100	105.0	100.00	110.0	100.00	115.0	100.00	120.0	100.00

* this composition has been obtained using WERAMI 1 for the pseudosection calculated using the actually measured bulk composition
** this is the measured bulk composition

Start adding a small amount of melt (0.05 mol%); use the new "melt-reintegrated" bulk composition to calculate a new pseudosection and check if the *solidus* is dry or wet.

Repeat this process for progressively increasing amounts of melt reintegrated to the measured bulk composition and check the nature of the *solidus* each time.

The pseudosection calculated using the bulk composition obtained by re-integration of 0.20 mol% of melt predicts a wet *solidus* over the entire pressure range of interest. This "melt-reintegrated" bulk composition should be therefore considered as the APPROXIMATE protolith composition.

You can use this "melt-reintegrated" pseudosection:
(a) to constrain the APPROXIMATE prograde evolution of your sample and,
(b) to estimate the MAXIMUM amount of melt that would have been produced if no melt loss occurred during the prograde evolution (i.e. if melt loss occurred in a single event, at peak P-T conditions).

Measured bulk composition

Melt-reintegrated bulk composition

Ex. 13

Ex. 13 – log$f$(S$_2$) vs log$f$(O$_2$) diagram for the system C-Fe

The aim of this exercise is to calculate a log$f$(S$_2$) vs. log$f$(O$_2$) diagram showing the stability fields of Fe-oxides, Fe-sulphides and graphite as a function of f(S$_2$) and f(O$_2$) (see the figure below; Best, 2003: "Igneous and metamorphic petrology", 2nd edition, Balckwell).

It is explained how to use CTRANSF for redefining the thermodynamic components of the database and how to deal with fugacities as independent variables. The diagram also shows compositional variations of the pyrrothite solid solution as a function of log$f$(S$_2$) and allows predicting fluid speciation as a function of log$f$(O$_2$) and log$f$(S$_2$).

16.30 Stability field of graphite compared with those of Fe-oxides and Fe-sulfides at $P = 2$ kbar, $P_{H_2O} = 1$ kbar, and 700°C. Redrawn from Froese (1981).

(1) Redefinition of the thermodynamic components (CTRANSF)

In order to consider the equilibria involving iron, Fe-sulphides, Fe-oxides, graphite, CO2 and CH4, we need to transform the database by redefining the thermodynamic components in term of Fe, C, O2 and H2 (instead of FeO, CO2 and H2O). This can be done by CTRANSF:

C = CO2-O2

O2=CO2-C

H2=H2O-0.5 O2
Fe = FeO – 0.5O2

Run CTRANSF:

C:\PERPLEX\Perplex686>ctransf

Perple_X version 6.8.6, source updated Jan 24, 2019.
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NO is the default answer to all Y/N prompts

Enter thermodynamic data file name [default = hp02ver.dat]:
hp62ver.dat

Output will be written to file: ctransf.dat

The current data base components are:
 Na2O MgO Al2O3 SiO2 K2O CaO TiO2 MnO FeO NiO ZrO2 Cl2 O2   H2O CO2 CuO Cr2O3 S2
F2
Transform them (Y/N)?
y
Enter new component name, < 6 characters, left justified:
C
Enter old component to be replaced with C   :
O2
Enter other components (< 11) in C   1 per line, <enter> to finish:
CO2

Enter stoichiometric coefficients of:
  O2   CO2
in C   (in above order):
-1
1
 C   = -1.00 O2   1.00 CO2
Is this correct (Y/N)?
y

The current data base components are:
 Na2O MgO Al2O3 SiO2 K2O CaO TiO2 MnO FeO NiO ZrO2 Cl2 C   H2O CO2 CuO Cr2O3 S2   F2
Transform them (Y/N)?
y
Enter new component name, < 6 characters, left justified:
O2
Enter old component to be replaced with O2   :
CO2

CO2   is a possible saturated phase component. Is the new component O2 also a possible saturated phase
component (Y/N)?

n

Enter other components (< 11) in O2   1 per line, <enter> to finish:

C

Enter stoichiometric coefficients of:
  CO2   C
in O2   (in above order):

1

-1

 O2   =   1.00 CO2   -1.00 C

Is this correct (Y/N)?

y

The current data base components are:

 Na2O MgO   Al2O3 SiO2 K2O   CaO   TiO2 MnO   FeO   NiO   ZrO2 Cl2 C   H2O   O2   CuO   Cr2O3 S2   F2

Transform them (Y/N)?

y

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

H2

Enter old component to be replaced with H2   :

H2O

H2O   is a possible saturated phase component. Is the new component H2 also a possible saturated phase component (Y/N)?

n

Enter other components (< 11) in H2   1 per line, <enter> to finish:

O2

Enter stoichiometric coefficients of:
  H2O   O2
in H2   (in above order):

1

-0.5

 H2   =   1.00 H2O   -0.50 O2

Is this correct (Y/N)?

y

The current data base components are:

 Na2O MgO   Al2O3 SiO2 K2O   CaO   TiO2 MnO   FeO   NiO   ZrO2 Cl2 C   H2   O2   CuO   Cr2O3 S2   F2

Transform them (Y/N)?

y

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

Fe

Enter old component to be replaced with Fe   :

FeO

Enter other components (< 11) in Fe   1 per line, <enter> to finish:

O2

Enter stoichiometric coefficients of:
  FeO O2
in Fe   (in above order):
1
-0.5
 Fe   = 1.00 FeO -0.50 O2
Is this correct (Y/N)?
y

The current data base components are:
 Na2O MgO Al2O3 SiO2 K2O CaO TiO2 MnO Fe   NiO ZrO2 Cl2 C   H2   O2   CuO Cr2O3 S2   F2
Transform them (Y/N)?
n

A new file **ctrans.dat** has been created in the Perplex folder. This is the equivalent of hp62ver.dat, but with the Fe, C, O2 and H2 components instead of FeO, CO2 and H2O. The file ctransf.dat should be specified as the thermodynamic data file in the following calculation.

(2) Definition of the problem (BUILD)

C:\PERPLEX\Perplex686>build

Perple_X version 6.8.6, source updated Jan 24, 2019.
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NO is the default (blank) answer to all Y/N prompts

Enter a name for this project (the name will be used as the root for all output file names) [default = my_project]:
ex13

The problem definition file will be named: ex13.dat

Enter thermodynamic data file name [default = hp02ver.dat]:
ctransf.dat
This is the new database.

Enter the computational option file name [default = perplex_option.dat]:
See: www.perplex.ethz.ch/perplex_options.html

Reading Perple_X options from: perplex_option.dat

The current data base components are:
The current data base components are:
 Na2O MgO Al2O3 SiO2 K2O CaO TiO2 MnO Fe   NiO ZrO2 Cl2 C   H2   O2   CuO Cr2O3 S2   F2
n

Note that Fe, C, O2 and H2 (and not FeO, CO2 and H2O) appear in the list of the database components.

Specify computational mode:
    1 - Convex-Hull minimization
    2 - Constrained minimization on a 2d grid [default]
    3 - Constrained minimization on a 1d grid
    4 - Output pseudocompound data
    5 - 1-d Phase fractionation
    6 - 0-d Infiltration-reaction-fractionation
    7 - 2-d Phase fractionation (FRAC2D and TITRATE reactive transport models)

Use Convex-Hull minimization for Schreinemakers projections or phase diagrams with > 2 independent variables. Use constrained minimization for phase diagrams or phase diagram sections with < 3 independent variables.

2

Although this type of calculation could be done with CONVEX (i.e. a $\log f(S_2)$ – $\log f(O_2)$ grid), it is preferable to treat it with VERTEX as a pseudosection (using a generic bulk composition such as: Fe=1, H2=1, C=0.5 mol%), because using a fluid model in CONVEX is costly in term of calculation time.

Calculations with saturated components (Y/N)?

n

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

y

We want to calculate a $\log f(S_2)$ vs $\log f(O_2)$ diagram, therefore we need to use fugacities as independent variables on both the axes.

Specify a component whose chemical potential, activity or fugacity is to be independent, press <enter> to finish:

Na2O MgO Al2O3 SiO2 K2O CaO TiO2 MnO Fe NiO ZrO2 Cl2 C   H2   O2   CuO Cr2O3 S2   F2

S2

Component S2   is to be characterized by:
    1 - chemical potential [default]
    2 - log10(fugacity)
    3 - log10(activity)

2

Select the phase to be used to define S2   fugacity from the following:
    S   S2

S2

warning ver064 in general it is wise to exclude the unused phases from the above list from your calculation. NOTE: you will not be prompted for these phases if you select the automatic phase exclusion prompt. to exclude unused reference phases either do not select the prompt option or edit the problem definition after running BUILD

Read this note. We must remember to exclude S by editing the input file.

The log10(S2   fugacity) variable is named: f_S2

Specify a component whose chemical potential, activity or fugacity is to be independent, press <enter> to finish:
In other words, if you only want one mobile component, then press <enter>
Na2O MgO Al2O3 SiO2 K2O CaO TiO2 MnO Fe NiO ZrO2 Cl2 C H2 O2 CuO Cr2O3 F2
O2

Component O2 is to be characterized by:
    1 - chemical potential [default]
    2 - log10(fugacity)
    3 - log10(activity)
2
Phase O2 will be used to define O2 fugacity
The log10(O2 fugacity) variable is named: f_O2

Select thermodynamic components from the set:
 Na2O MgO Al2O3 SiO2 K2O CaO TiO2 MnO Fe NiO ZrO2 Cl2 H2O C CuO Cr2O3 F2
Enter names, 1 per line, press <enter> to finish:
Fe
H2
C

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

Select x-axis variable:
    1 - P(bar)
    2 - T(K)
    3 - f_S2
    4 - f_O2
    5 - Composition X_C1* (user defined)
*X_C1 can not be selected as the y-axis variable
3

Enter minimum and maximum values, respectively, for: f_S2
-15
5
WARNING f_S2 is the base 10 log of activity/fugacity; therefore f_S2 implies supersaturation with respect to the reference phase.
Specify new values (Y/N)?
n

Select y-axis variable:
    2 - T(K)
    3 - P(bar)
    4 - f_O2
4

Enter minimum and maximum values, respectively, for: f_O2

-25

-5

Specify sectioning value for: P(bar)

2000

Specify sectioning value for: T(K)

973

For gridded minimization, grid resolution is determined by the number of levels (grid_levels) and the resolution at the lowest level in the X- and Y-directions (x_nodes and y_nodes) these parameters are currently set for the exploratory and autorefine cycles as follows:

stage	grid_levels	xnodes	ynodes	effective resolution
exploratory	1	40	40	40 x 40 nodes
auto-refine	4	60	60	473 x 473 nodes

To change these options edit or create the file perplex_option.dat
See: www.perplex.ethz.ch/perplex_options.html#grid_parameters

Specify component amounts by mass (Y/N)?

n

The amounts you enter next need not be normalized; regardless of units, they define the molar amount of the system

Enter the molar amounts of the components:
 Fe   H2   C
for the bulk composition of interest:

1

1

0.5

warning ver110 in this mode Perple_X will not check whether conditions are supersaturated with respect to mobile components.
To explicitly compute saturation surfaces:
  1) use convex hull optimization and do not use activities or fugacities as independent variables
  2) or compute the saturation surface with FLUIDS or FRENDLY.

Output a print file (Y/N)?

y

warning ver051 cannot make hmjL   because of missing data or an invalid definition in the thermodynamic data file.
…

Exclude pure and/or endmember phases (Y/N)?

Y

Do you want to be prompted for phases (Y/N)?

y

Exclude fper   (Y/N)?

y

Exclude hem   (Y/N)?

n

Exclude mt   (Y/N)?

n

Exclude gth   (Y/N)?

y

Exclude sid   (Y/N)?

n

Exclude pyr   (Y/N)?

n

Exclude trot   (Y/N)?

N

Exclude tro   (Y/N)?

y

Exclude lot   (Y/N)?

y

Exclude trov   (Y/N)?

N

The pyrrothite solution model is defined by two end-members: **trot (FeS)** and **trov (Fe$_{0.88}$S)**. tro and lot should be excluded.

Exclude iron   (Y/N)?

n

Exclude gph   (Y/N)?

n

Exclude diam   (Y/N)?

y

Exclude H2O   (Y/N)?

n

Exclude CO2   (Y/N)?

n

Exclude CO   (Y/N)?

Y

You can exclude CO to speed up the calculation.

Exclude CH4   (Y/N)?

n

Exclude H2   (Y/N)?

n

Exclude H2S   (Y/N)?

n

Exclude h2oL   (Y/N)?

y

Exclude fbr   (Y/N)?

y

Include solution models (Y/N)?

y

Enter the solution model file name [default = solution_model.dat]:

enter

…

Select models from the following list, enter 1 per line, press <enter> to finish

electrolytic_fluid models Aq_yuri   Aq_solven0

fluid models: F   F(salt)   COHF   COH-Fluid COH-Fluid+

              WADDAH   C-H-Fluid HOS-Fluid

pyrrhotite models: Po(HP)

gas models: CCO-vapor

For details on these models see: www.perplex.ethz.ch/perplex_solution_model_glossary.html or read the commentary in the solution model file.

COH-Fluid

Po(HP)

Enter calculation title:

Ex13

(3) Doing the calculation (VERTEX)

Before running CONVEX, remember to edit the input file by excluding "S".

Run CONVEX to make the calculation:

C:\PERPLEX\Perplex686>vertex

Perple_X version 6.8.6, source updated Jan 24, 2019.
Copyright (C) 1986-2019 James A D Connolly <www.perplex.ethz/copyright.html>.

Enter the project name (the name assigned in BUILD) [default = my_project]:

ex13

…

…

(4) Plotting the calculated phase diagram (PSSECT)

Run PSSECT to plot the calculated phase diagram.

C:\PERPLEX\Perplex686>pssect

Perple_X version 6.8.6, source updated Jan 24, 2019.
Copyright (C) 1986-2019 James A D Connolly <www.perplex.ethz/copyright.html>.

Enter the project or plot file name [i.e., without the .plt suffix]:

ex13

Perple_X plot options are currently set as:
   Keyword: Value: Permitted values [default]:
   axis_label_scale   1.20   [1.2] (rel)

bounding_box :
              0   [0] x-min (pts)
              0   [0] y-min (pts)
           800   [800] x-length (pts)
           800   [800] y-length (pts)
field_fill   T   [T] F
field_label   T   [T] F
field_label_scale 0.75   [0.72] (rel)
font   Helvetica
grid   F   [F] T
half_ticks   T   [T] F
line_width   1.00   0-99 [1.] (pts)
picture_transformation :
          0.180   [0.18] x-scale (rel)
          0.180   [0.18] y-scale (rel)
          130.   [0.18] x-translation (pts)
          220.   [0.18] y-translation (pts)
          0.00   [0.0] rotation (deg)
plot_aspect_ratio 1.000   [1.0] x_axis_length/y_axis_length
replicate_label 0.250   0->1 [0.025]
splines   T   [T] F
tenth_ticks   F   [F] T
text_scale   1.000   [1.] (rel)
To change these options edit or create the plot option file
See: www.perplex.ethz.ch/perplex_plot_options.html

PostScript will be written to file: ex13.ps

Modify the default plot (y/n)?
n

(5) Calculating fluid speciation and pyrrothite composition (WERAMI)

Fluid speciation (for the specified P-T conditions and system composition) and pyrrothite composition as a function of f(S_2) and f(O_2) can be calculated using WERAMI.

C:\PERPLEX\Perplex686>werami

Perple_X version 6.8.6, source updated Jan 24, 2019.
Copyright (C) 1986-2019 James A D Connolly <www.perplex.ethz/copyright.html>.

Enter the project name (the name assigned in BUILD) [default = my_project]:
ex13

Reading Perple_X options from: perplex_option.dat
Writing Perple_X option summary to file: not requested

Perple_X version 6.8.6, source updated Jan 24, 2019.
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Perple_X computational option settings for WERAMI:
  Keyword: Value: Permitted values [default]:
 Input/Output options:

  aqueous_output   T   [F] T
  aqeuous_species   20   [20] 0-100
  aq_solvent_composition y   [y] m: y => mol fraction, m => molality
  aq_solute_composition m   y [m]: y => mol fraction, m => molality

```
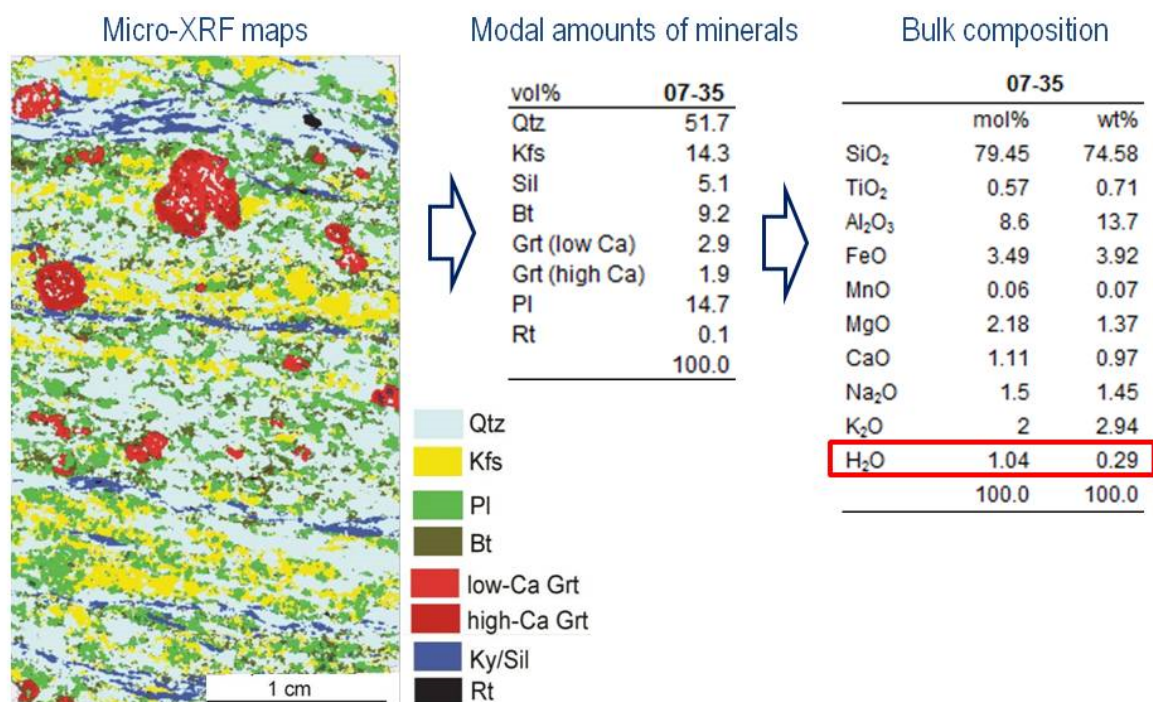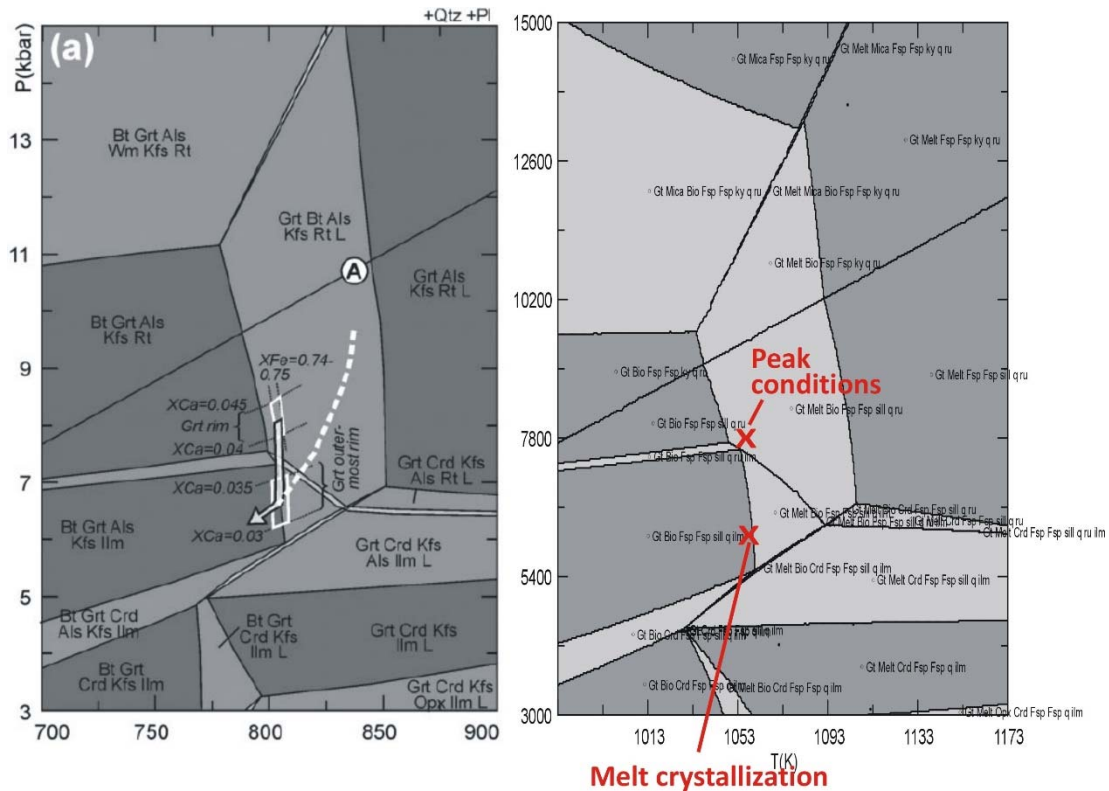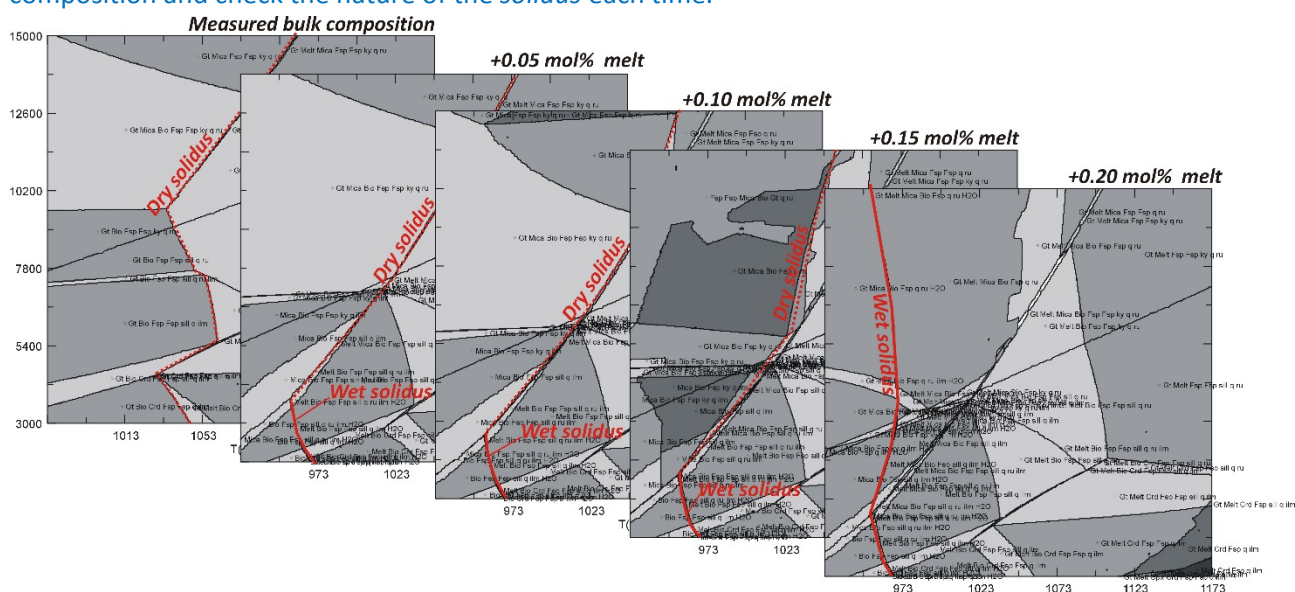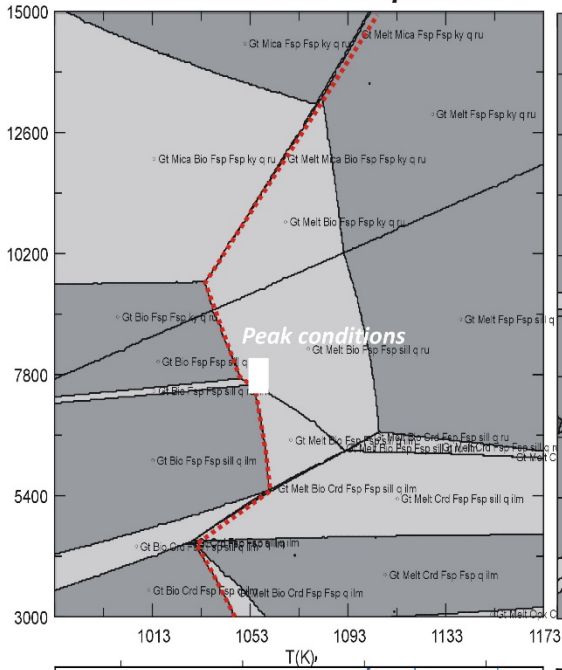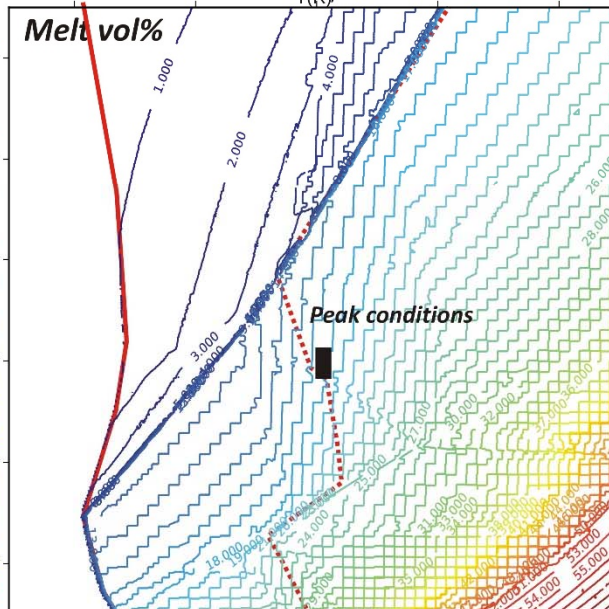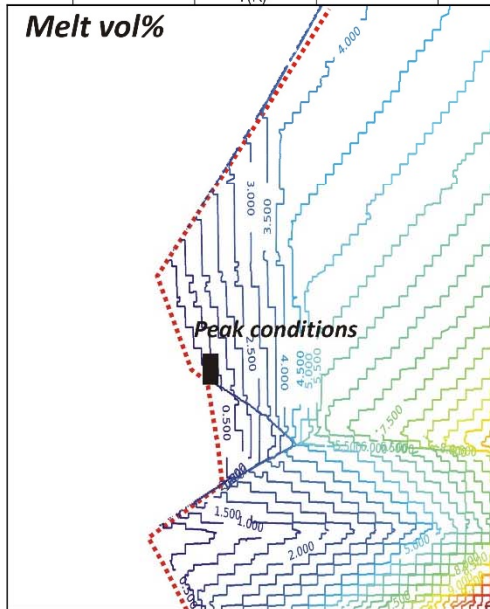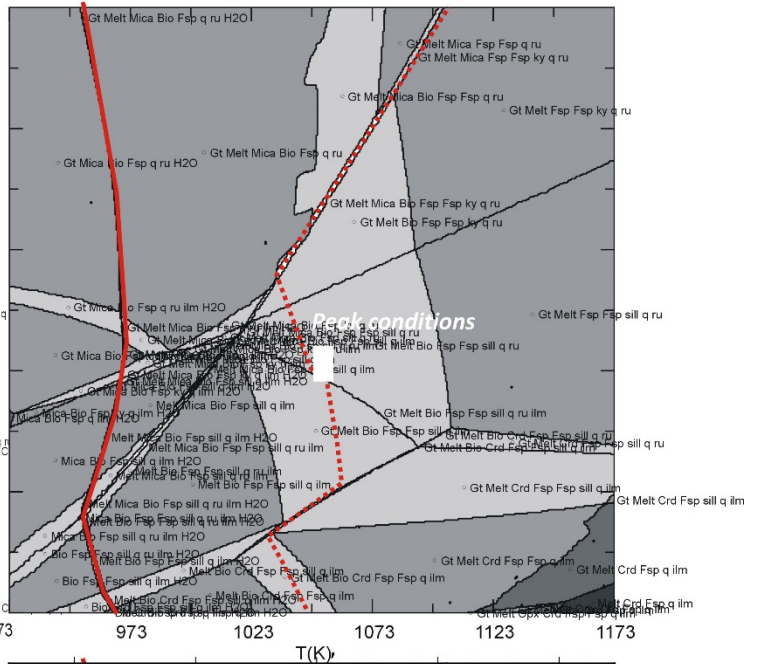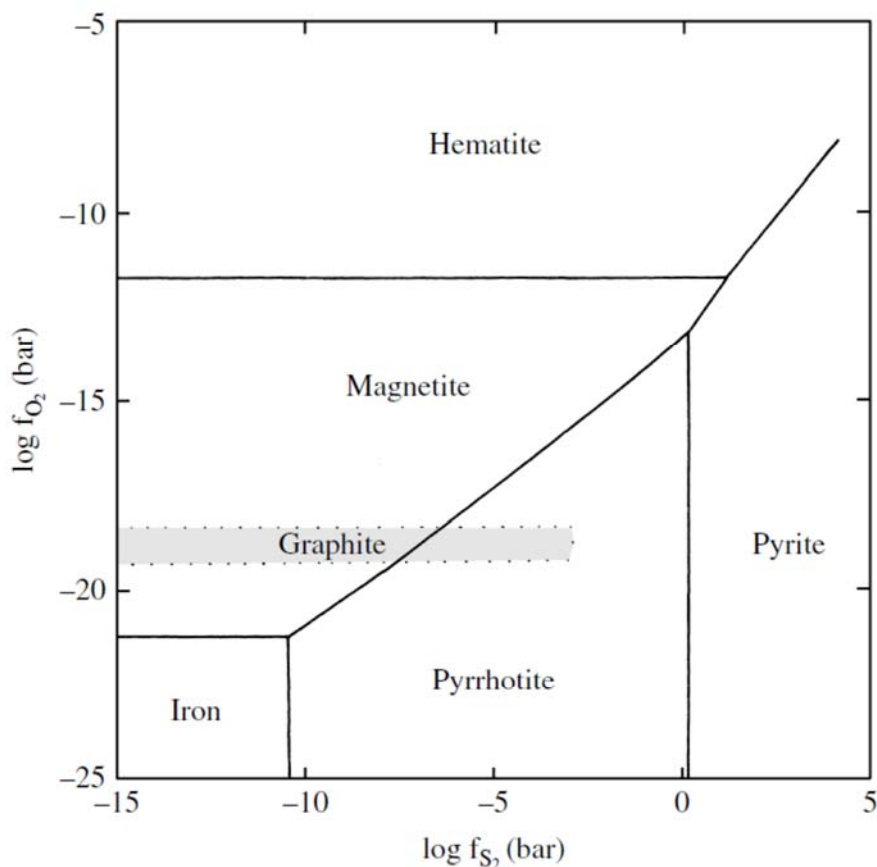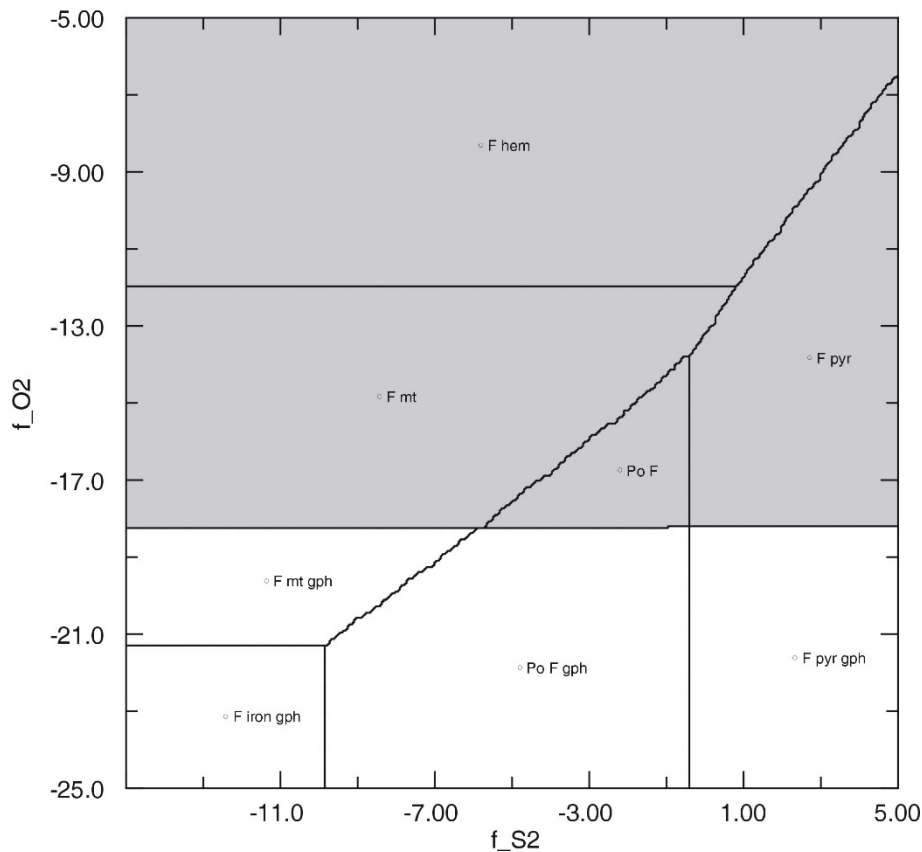spreadsheet          T         [F] T
logarithmic_p        F         [F] T
bad_number           NaN       [NaN]
composition_constant  F        [F] T
composition_phase    mol       [mol] wt
composition_system   wt        [wt] mol
proportions          vol       [vol] wt mol
absolute             F         [F] T
cumulative           F         [F] T
fancy_cumulative_modes F       [F] T
interpolation        on        [on] off
melt_is_fluid        F         [F] T
solution_names       abb       [model] abbreviation full
species_output       T         [T] F
species_Gibbs_energies F       [F] T
seismic_output       som       [some] none all
pause_on_error       T         [T] F
poisson_test         F         [F] T
interim_results      aut       [auto] off manual
sample_on_grid       F         [T] F
auto_exclude         T         [T] F
 Information file output options:
  option_list_files   F        [F] T; echo computational options
 Thermodynamic options:
  approx_alpha        T        [T] F
  Anderson-Gruneisen  F        [F] T
  hybrid_EoS_H2O      4        [4] 0-2, 4-7
  hybrid_EoS_CO2      4        [4] 0-4, 7
  hybrid_EoS_CH4      0        [0] 0-1, 7
  fd_expansion_factor 2.0      >0 [2]
  finite_difference_p  0.1D+05  >0 [1d4]; fraction = 0.1D-02  [1d-2]
 Seismic velocity options:
  bounds              VRH      [VRH] HS
  vrh/hs_weighting    0.5      [0.5] 0->1
  explicit_bulk_modulus T      [F] T
  poisson_ratio       on       [on] all off; Poisson ratio = 0.35
To change these options see: www.perplex.ethz.ch/perplex_options.html

Select operational mode:
   1 - properties at specified conditions
   2 - properties on a 2d grid
   3 - properties along a 1d path
   4 - as in 3, but input from file
   0 - EXIT
2


Select a property [enter 0 to finish]:
   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 - Composition (Mol, Mass, or Wt%) of the system

7 - Mode (Vol, Mol, or Wt proportion) of a phase

8 - Composition (Mol, Mass, or Wt%) of a solution phase

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-system)

21 - Poisson ratio

22 - Molar Volume (J/bar)

23 - Dependent potentials (J/mol, bar, K)

24 - Assemblage Index

25 - Modes of all phases

26 - Sound velocity T derivative (km/s/K)

27 - P-wave velocity T derivative (km/s/K)

28 - S-wave velocity T derivative (km/s/K)

29 - Adiabatic bulk modulus T derivative (bar/K)

30 - Shear modulus T derivative (bar/K)

31 - Sound velocity P derivative (km/s/bar)

32 - P-wave velocity P derivative (km/s/bar)

33 - S-wave velocity P derivative (km/s/bar)

34 - Adiabatic bulk modulus P derivative (unitless)

35 - Shear modulus P derivative (unitless)

36 - All phase &/or system properties

37 - Absolute amount (Vol, Mol, or Wt) of a phase

38 - Multiple property output

39 - Heat capacity ratio (Cp/Cv)

40 - Lagged or back-calculated aqueous solute chemistry

8

Enter solution (left justified):

COH-Fluid

Define the composition in terms of the species/endmembers of COH-Fluid (y/n)?

Answer no to define a composition in terms of the systems components.

Units (mass or molar) are controlled by the composition keyword in perplex_option.dat.

y

Compositions are defined as a ratio of the form:

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

        y(j)   = mole fraction of species j

w(j)   = weighting factor of species j (usually 1)

How many species in the numerator of the composition (<13)?
1

Enter species indices and weighting factors for the numerator:
   1 - CO2
   2 - CH4
   3 - H2S
   4 - H2
   5 - H2O
1
1

How many species in the denominator of the composition (<12)?
Enter zero to use the numerator as a composition.
0

The compositional variable is: 1.0 CO2

Change it (y/n)?
n

This composition will be designated: C[COH-Fluid1]

Select a property [enter 0 to finish]:
8

Enter solution (left justified):
COH-Fluid

Define the composition in terms of the species/endmembers of COH-Fluid (y/n)?

Answer no to define a composition in terms of the systems components.
Units (mass or molar) are controlled by the composition keyword in perplex_option.dat.
y

Compositions are defined as a ratio of the form:
    Sum {w(i)*n(i), i = 1, c1} / Sum {w(i)*y(i), i = c2, c3}
        y(j)   = mole fraction of species j
        w(j)   = weighting factor of species j (usually 1)

How many species in the numerator of the composition (<13)?
1

Enter species indices and weighting factors for the numerator:
   1 - CO2
   2 - CH4
   3 - H2S
   4 - H2

5 - H2O
2
1

How many species in the denominator of the composition (<12)?
Enter zero to use the numerator as a composition.
0

The compositional variable is: 1.0 CH4

Change it (y/n)?
n

This composition will be designated: C[COH-Fluid2]

Select a property [enter 0 to finish]:
8

Enter solution (left justified):
COH-Fluid

Define the composition in terms of the species/endmembers of COH-Fluid (y/n)?

Answer no to define a composition in terms of the systems components.
Units (mass or molar) are controlled by the composition keyword in perplex_option.dat.
y

Compositions are defined as a ratio of the form:
   Sum {w(i)*n(i), i = 1, c1} / Sum {w(i)*y(i), i = c2, c3}
       y(j)   = mole fraction of species j
       w(j)   = weighting factor of species j (usually 1)

How many species in the numerator of the composition (<13)?
1

Enter species indices and weighting factors for the numerator:
   1 - CO2
   2 - CH4
   3 - H2S
   4 - H2
   5 - H2O
3
1

How many species in the denominator of the composition (<12)?
Enter zero to use the numerator as a composition.
0

The compositional variable is: 1.0 H2S

Change it (y/n)?
n

This composition will be designated: C[COH-Fluid3]

Select a property [enter 0 to finish]:
8

Enter solution (left justified):
COH-Fluid

Define the composition in terms of the species/endmembers of COH-Fluid (y/n)?

Answer no to define a composition in terms of the systems components.
Units (mass or molar) are controlled by the composition keyword in perplex_option.dat.
y

Compositions are defined as a ratio of the form:
    Sum {w(i)*n(i), i = 1, c1} / Sum {w(i)*y(i), i = c2, c3}
        y(j)   = mole fraction of species j
        w(j)   = weighting factor of species j (usually 1)

How many species in the numerator of the composition (<13)?
1

Enter species indices and weighting factors for the numerator:
  1 - CO2
  2 - CH4
  3 - H2S
  4 - H2
  5 - H2O
4
1

How many species in the denominator of the composition (<12)?
Enter zero to use the numerator as a composition.
0

The compositional variable is: 1.0 H2

Change it (y/n)?
n

This composition will be designated: C[COH-Fluid4]

Select a property [enter 0 to finish]:
8

Enter solution (left justified):
COH-Fluid

Define the composition in terms of the species/endmembers of COH-Fluid (y/n)?

Answer no to define a composition in terms of the systems components.
Units (mass or molar) are controlled by the composition keyword in perplex_option.dat.
y

Compositions are defined as a ratio of the form:
    Sum {w(i)*n(i), i = 1, c1} / Sum {w(i)*y(i), i = c2, c3}
        y(j) = mole fraction of species j
        w(j) = weighting factor of species j (usually 1)

How many species in the numerator of the composition (<13)?
1

Enter species indices and weighting factors for the numerator:
    1 - CO2
    2 - CH4
    3 - H2S
    4 - H2
    5 - H2O
5
1

How many species in the denominator of the composition (<12)?
Enter zero to use the numerator as a composition.
0

The compositional variable is: 1.0 H2

Change it (y/n)?
n

This composition will be designated: C[COH-Fluid5]

Select a property [enter 0 to finish]:
8

Enter solution (left justified):
Po(HP)

Define the composition in terms of the species/endmembers of Po(HP)   (y/n)?

Answer no to define a composition in terms of the systems components.
Units (mass or molar) are controlled by the composition keyword in perplex_option.dat.
y

Compositions are defined as a ratio of the form:
    Sum {w(i)*n(i), i = 1, c1} / Sum {w(i)*y(i), i = c2, c3}
        y(j) = mole fraction of species j

w(j) = weighting factor of species j (usually 1)

How many species in the numerator of the composition (<13)?
1

Enter species indices and weighting factors for the numerator:
  1 - trov
  2 - trot
1
1

How many species in the denominator of the composition (<12)?
Enter zero to use the numerator as a composition.
0

The compositional variable is: 1.0 trov

Change it (y/n)?
n

This composition will be designated: C[Po(HP)6]

Select a property [enter 0 to finish]:
0

n

Select the grid resolution (to use an arbitrary grid set sample_on_grid to F):
  1 -   60 x   60 nodes
  2 - 119 x 119 nodes
  3 - 237 x 237 nodes
  4 - 473 x 473 nodes [default]
4

warning ver178 at T(K)= 973.0   P(bar)= 2000.
the shear modulus of: iron is missing or invalid and has been estimated from the default poisson ratio
…
…

Data ranges excluding values equal to bad_number (NaN) specified in perplex_option.dat:
   C[COH-Fluid1] C[COH-Fluid2] C[COH-Fluid3] C[COH-Fluid4] C[COH-Fluid5] C[Po(HP)6]
min   0.00000   0.00000   0.00000   0.00000   0.00000   0.199653E-001
max 0.333333   0.950521   1.00000   0.486111E-001 0.486111E-001 1.00000

Output has been written to the 2d tab format file: EX13_1.tab

2d tab format files can be processed with:
   PSTABLE - a Perple_X plotting program
   PERPLE_X_PLOT - a MATLAB plotting script
   PYWERAMI - github.com/ondrolexa/pywerami
   spread-sheet programs, e.g., EXCEL

for details on tab format refer to: perplex.ethz.ch/perplex/faq/Perple_X_tab_file_format.txt

Select operational mode:
   1 - properties at specified conditions
   2 - properties on a 2d grid
   3 - properties along a 1d path
   4 - as in 3, but input from file
   0 - EXIT
0

The dashed fields represent unrealistic conditions (almost pure H2S or CH4 fluid, in blue and red, respectively). The **stability field of graphite in equilibrium with a C-O-H fluid is represented in white**. The coexistence of graphite and magnetite or pyrrothite strongly constrains the oxidation conditions of the system.