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 6.8.9** (released on January 31, 2020). 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

Ex 6: T-XMg section for the $CaCO_3$-$MgCO_3$ system (solvus relations) Pag. 83

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.

Ex 7: P-T projection for the $CaCO_3$-$MgCO_3$ system using solid solutions Pag. 98

This exercise explains how to calculate a P-T projection for the $CaCO_3$-$MgCO_3$ 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.

Working with solid solutions in a more complex system

Ex 8: AFM chemographies in the KFMASH system Pag. 114

This exercise explains how to calculate the "classical" Thompson AFM diagrams for metapelites in the KFMASH system. Opposite to Ex. 3, solid solutions are here considered. The concept of **COMPONENT TRANSFORMATION** is introduced in order to create the three new components: MU = 0.5 K2O + 1.5 Al2O3, PHL = 1.5 MgO – 0.5Al2O3 and ANN = 1.5 FeO – 0.5Al2O3.

Ex 9: P-T pseudosection for a METAPELITE in the KFMASH system Pag. 127

This exercise explains how to calculate a P-T pseudosection for a metapelite sample in the simplified KFMASH system, using solid solutions. The influence of other components (Na_2O, CaO and MnO) will be considered in the next exercise (Ex. 10). At the end, some **PRACTICAL TIPS FOR REDRAWING** the PerpleX outputs are given, and the comparison with the AFM chemographies calculated in Ex. 8 will be done. The second part of this exercise explains **how to calculate ISOMODES and compositional ISOPLETHS**.

Ex 10: P-T pseudosection for a METAPELITE in the MnNKCFMASH system Pag. 101

This exercise is intended to explore the influence of some minor components (Na_2O, CaO and MnO) on the topology of the pseudosection calculated for the metapelite sample investigated in Ex. 9. The exercise also explains **how to calculate CUMULATIVE MODES ALONG A GEOTHERMAL GRADIENT**.

Ex 11: T-XMg pseudosection for a METAPELITE in the MnNKCFMASH system Pag. 101

This exercise is intended to explore the influence of bulk XMg [MgO/(MgO+FeO)] on the stability fields of the main mineral assemblages, for the same metapelite sample investigated in Ex. 9 and 10. 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).

Modelling a melt-bearing system

Ex 1

Ex. 1 – P-T projection for the Al_2SiO_5 system

This exercise explains how to calculate a P-T diagram for the very simple, two-components system SiO_2-Al_2O_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\Perplex689>build

Perple_X version 6.8.9, source updated Jan 30, 2020.
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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 HP (Holland & Powell) databases are the most used in metamorphic petrology. 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 (from the THERMOCALC version TC-DS62; Holland & Powell, 2011).

More information about the HP databases are given at https://hpxeosandthermocalc.org/the-hpx-eos/

```
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 Fe_2O_3 from the components FeO and O_2 (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 alumino-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 SiO_2 as a saturated component.
NB. If more than one saturated component is specified, Perple_X applies the constraints sequentially, e.g., if Al_2O_3 and SiO_2 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\Perplex689>convex
```

```
Perple_X version 6.8.9, source updated Jan 30, 2020.
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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 problem definition from file: ex1.dat
Reading thermodynamic data from file: hp02ver.dat
Writing print output to file: ex1.plt
Writing plot output to file: ex1.plt
Reading solution models from file: not requested
Reading Perple_X options from: perplex_option.dat
Writing complete reaction list to: not requested
Writing Perple_X option summary to: not requested
```

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          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]
  non_linear_switch      F          [F] T
  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   on         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
--------------------------------------------------------------------------------
Summary of make-definition entities:
  sil8L    q8L
--------------------------------------------------------------------------------
--------------------------------------------------------------------------------
Summary of saturated-component entities:
```

```
 for: SIO2
  q       trd     crst     coe      stv      qL  qGL
  q       trd     crst     coe      stv      qL  qGL      q8L
--------------------------------------------------------------------------------
** Starting auto_refine computational stage **
Initial number of divariant assemblages to be tested is:     1
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\Perplex689>psvdraw

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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)
```
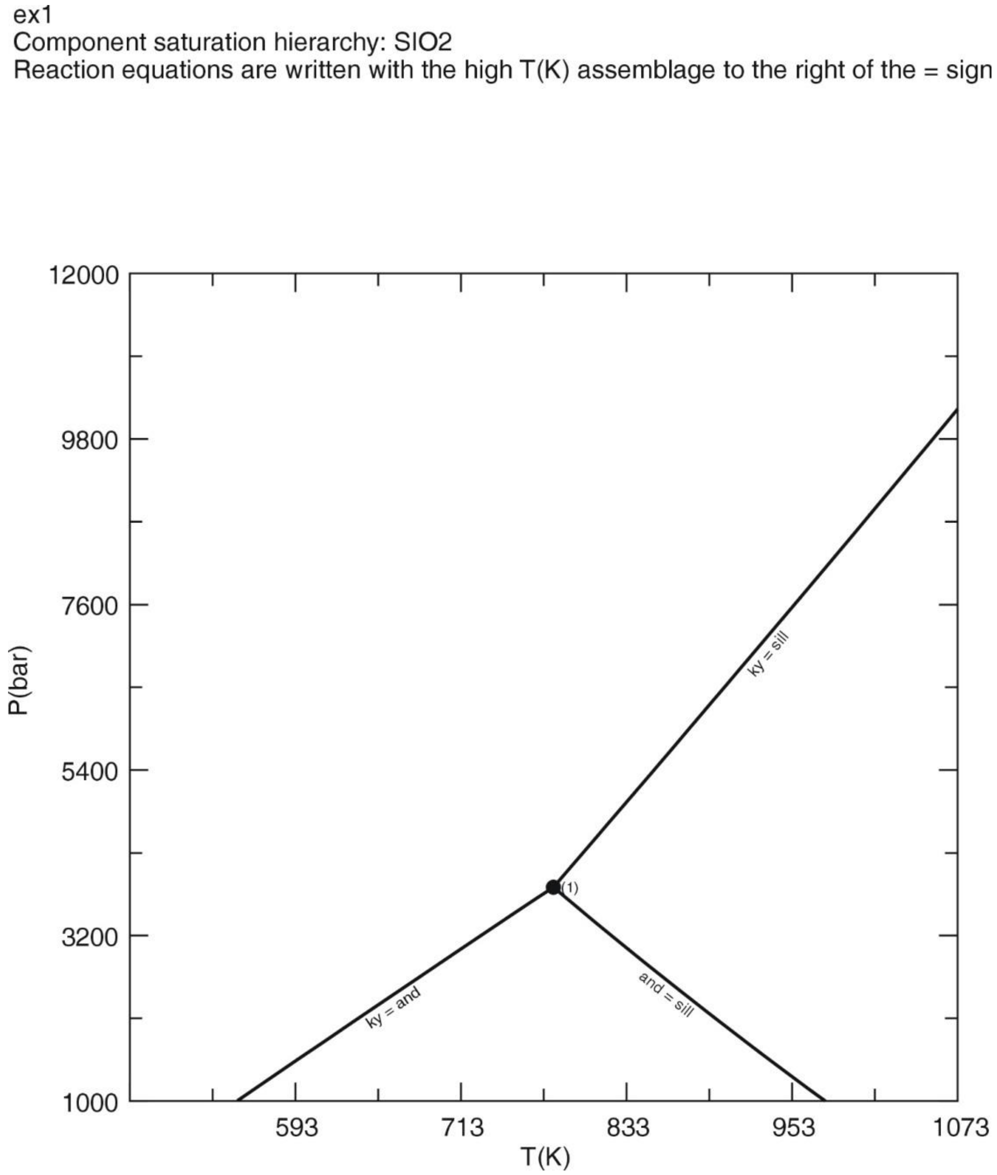

```
 plot_aspect_ratio      1.000      [1.0] x_axis_length/y_axis_length
 replicate_label       0.250      0->1 [0.025]
 splines              T         [T] F
 tenth_ticks           F         [F] T
 text_scale           1.000      [1.] (rel)

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.



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\Perplex689>psvdraw

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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

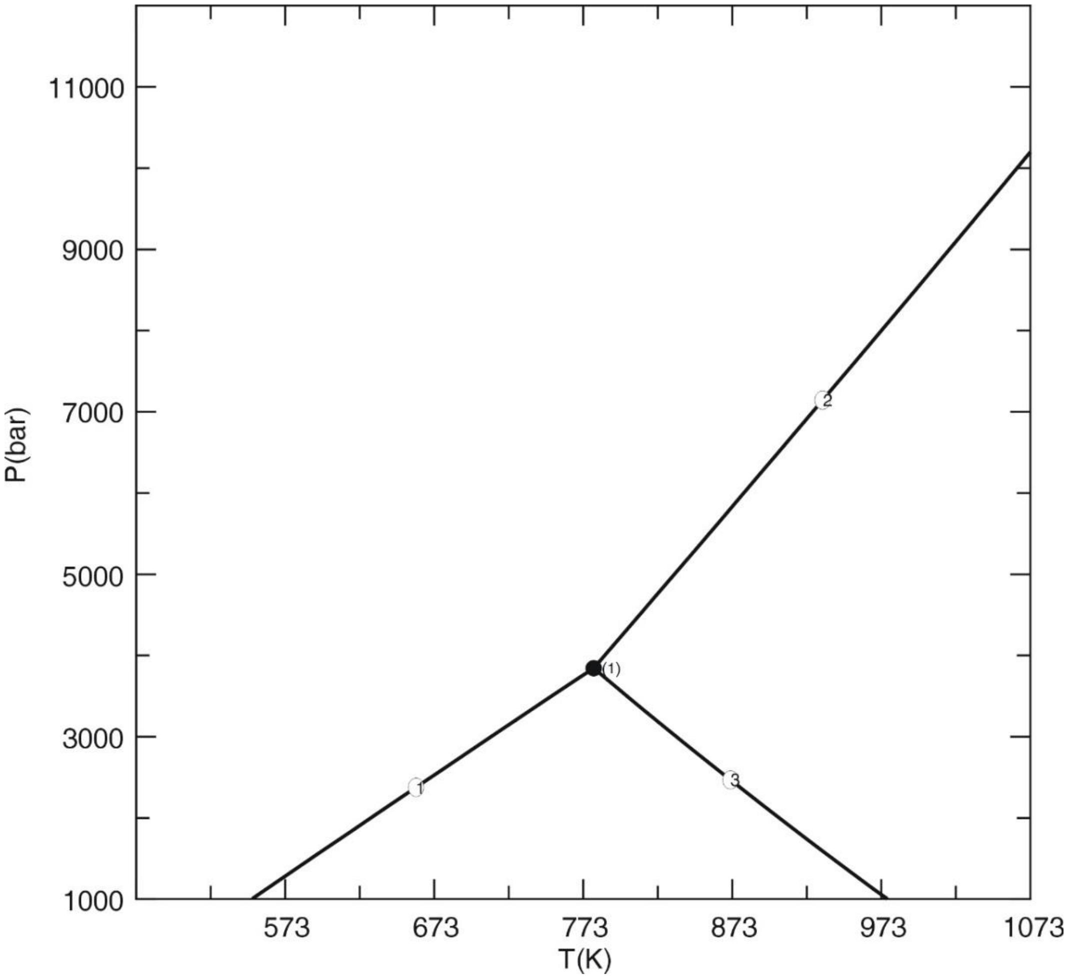
Enter minimum fraction of the axes length that a curve must be to receive a numeric label (0-1.000):
0 means that a numeric label will be assigned to all those curves that are shorter than the axes length.
0

```
Suppress point labels (y/n)?
n

Modify default axes numbering (y/n)?
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
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** to **hp62ver.dat**.

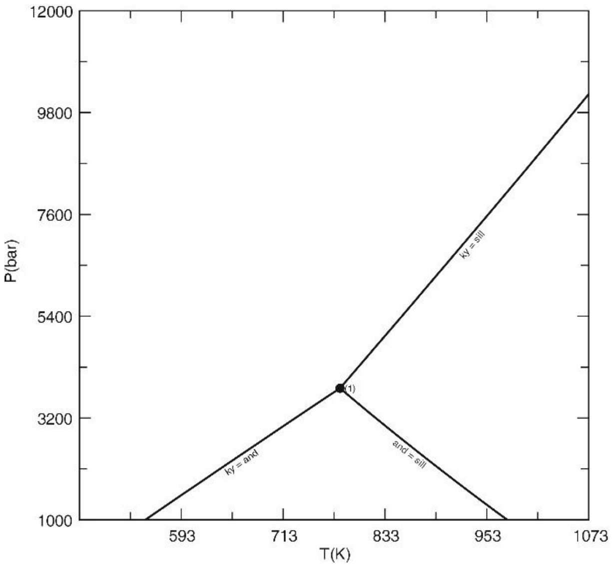
```
hp62ver.dat     thermodynamic data file
```

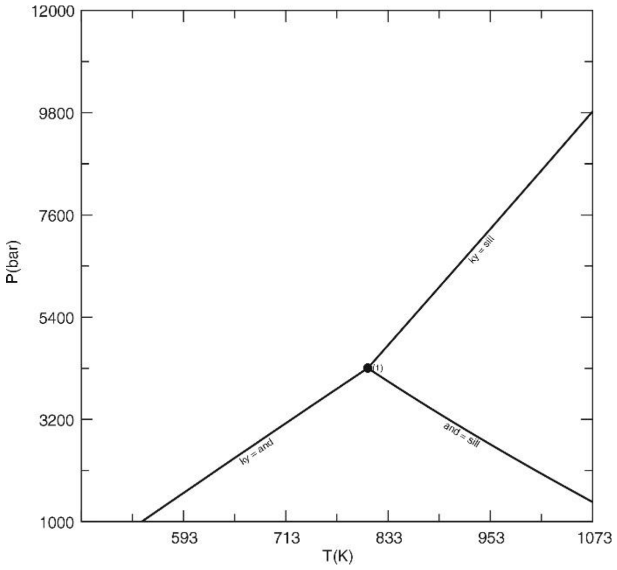
The most recent databases such as hp62ver.dat, define thermodynamic components with both upper and lower case characters (e.g. SiO2, Al2O3 etc.), opposite to the old databases, in which thermodynamic components were defined with upper case characters only (e.g. SIO2, AL2O3 etc.).
In the input file, change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

Save the file and run again CONVEX and PSVDRAW; 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 (no solid solutions)

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\Perplex689>build

Perple_X version 6.8.9, source updated Jan 31, 2020.
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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 TC-DS62; Holland & Powell, 2011). I suggest using the hp62ver.dat database, which has been tested in the last years and has demonstrated to be reliable for both metapelitic and metabasic systems. More information about the HP databases are given at https://hpxeosandthermocalc.org/the-hpx-eos/

```
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 N2 ZnO
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. 12 and Ex. 13***).

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  N2 ZnO
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

Having included only H2O as saturated fluid component, XCO2 is 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**.

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 and may result metastable at low-T.

rnk	rankinite Ca3Si2O7
lrn	larnite Ca2SiO4
cstn	“Si-titanite” CaSi2O5 (one Si replaces Ti)
wo	wollastonite CaSiO3
pswo	pseudo-wollastonite CaSiO3
wal	wollastonite CaSiO3
ak	akermanite Ca2MgSi2O7
merw	merwinite Ca3MgSi2O8
mont	monticellite CaMgSiO4
chum	clinohumite Mg9Si4O16(OH)2
cen	clinoenstatite Mg2Si2O6
cumm	cummingtonite Mg7Si8O22(OH)2
cumm_dqf	cummingtonite for Diener et al. (2007) cAmph model
woL	wollastonite LIQUID
limL	lime LIQUID
mcpv	make definitions for Holland et al., 2013 mantle mineralogical model
cmpv	make definitions for Holland et al., 2013 mantle mineralogical model
cpv	make definitions for Holland et al., 2013 mantle mineralogical model

As a general rule, however, it is always better not to exclude a priori any phase.

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\Perplex689>convex

Perple_X version 6.8.9, source updated Jan 31, 2020.
Copyright (C) 1986-2020 James A D Connolly <www.perplex.ethz/copyright.html>.

Enter the project name (the name assigned in BUILD) [default = my_project]:
Ex2

Reading problem definition from file: ex2.dat
Reading thermodynamic data from file: hp633ver.dat
Writing print output to file: ex2.plt
Writing plot output to file: ex2.plt
Reading solution models from file: not requested
Reading Perple_X options from: perplex_option.dat
Writing complete reaction list to: not requested
Writing Perple_X option summary to: not requested

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]
  non_linear_switch    F          [F] T
  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   on        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
------------------------------------------------------------------------------
Summary of make-definition entities:
    fo8L     q8L      cenjh    odi      qjL      dijL
    fojL     foTL     foHL     qHL
------------------------------------------------------------------------------
```

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\Perplex689>psvdraw

Perple_X version 6.8.9, source updated Jan 31, 2020.
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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
```
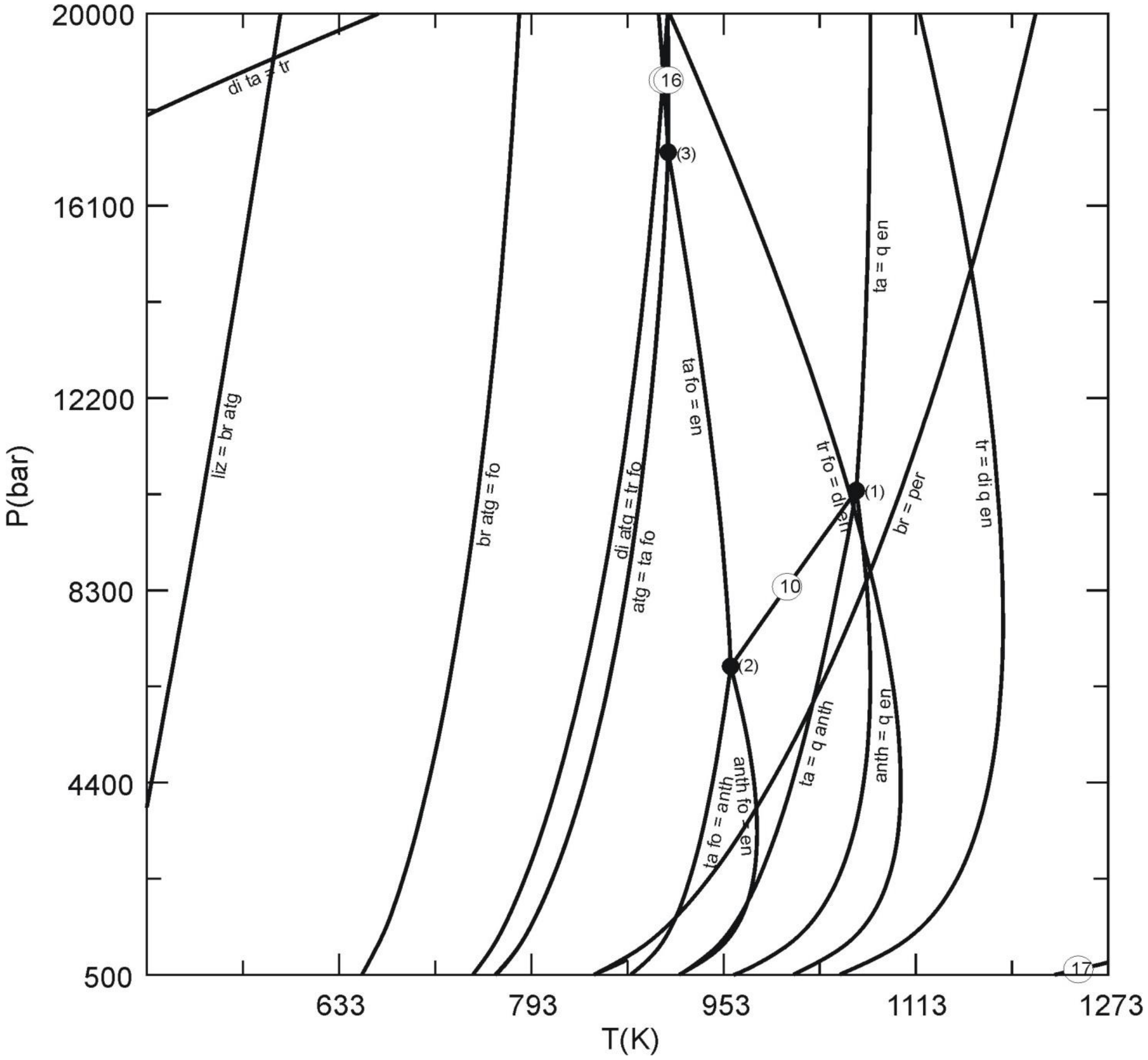

```
  tenth_ticks          F        [F] T
  text_scale           1.000      [1.] (rel)

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\Perplex689>psvdraw

Perple_X version 6.8.9, source updated Jan 31, 2020.
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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:

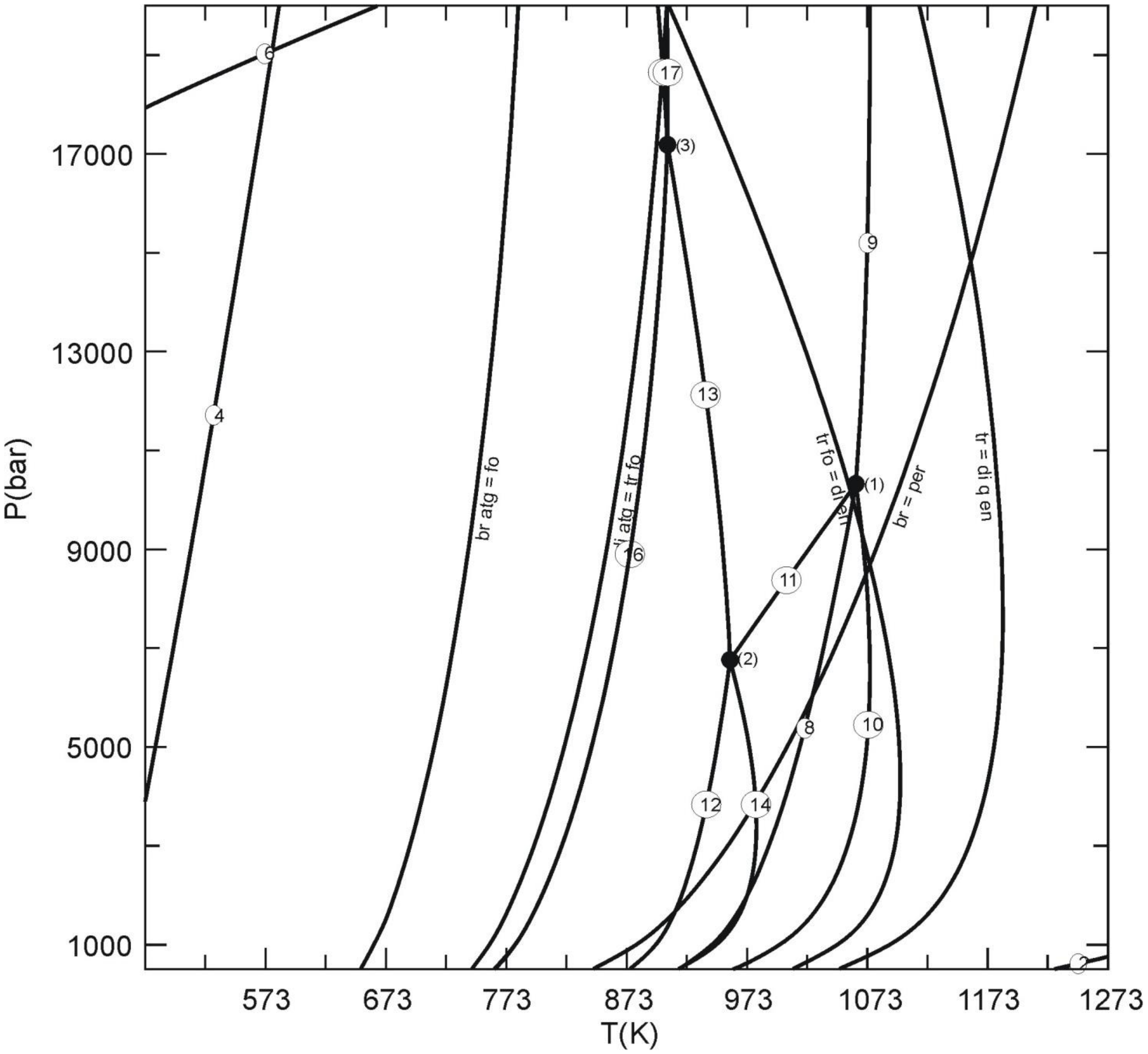
473

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

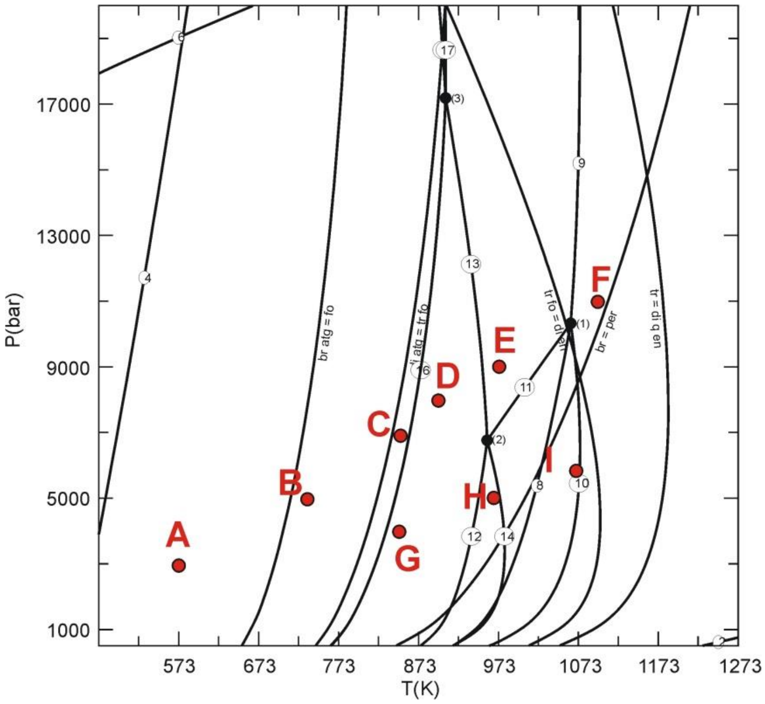


Equilibria corresponding to each reaction number are explained in the ex2.prn file.

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\Perplex689>build

Perple_X version 6.8.9, source updated Jan 31, 2020.
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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 N2 ZnO
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  N2
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

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 Ex. 2

rnk	rankinite Ca3Si2O7
lrn	larnite Ca2SiO4
cstn	“Si-titanite” CaSi2O5 (one Si replaces Ti)
wo	wollastonite CaSiO3
pswo	pseudo-wollastonite CaSiO3
wal	wollastonite CaSiO3
ak	akermanite Ca2MgSi2O7
merw	merwinite Ca3MgSi2O8
mont	monticellite CaMgSiO4
chum	clinohumite Mg9Si4O16(OH)2
cen	clinoenstatite Mg2Si2O6
cumm	cummingtonite Mg7Si8O22(OH)2
cumm_dqf	cummingtonite for Diener et al. (2007) cAmph model
woL	wollastonite LIQUID
limL	lime LIQUID
mcpv	make definitions for Holland et al., 2013 mantle mineralogical model
cmpv	make definitions for Holland et al., 2013 mantle mineralogical model
cpv	make definitions for Holland et al., 2013 mantle mineralogical model

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\Perplex689>convex

Perple_X version 6.8.9, source updated Jan 31, 2020.
Copyright (C) 1986-2020 James A D Connolly <www.perplex.ethz/copyright.html>.
```

```
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: hp633ver.dat
Writing print output to file: ex3.plt
Writing plot output to file: ex3.plt
Reading solution models from file: not requested
Reading Perple_X options from: perplex_option.dat
Writing Perple_X option summary to: not requested

Perple_X computational option settings for CONVEX:
    Keyword:          Value:    Permitted values [default]:
 Auto-refine options:
  auto_refine         aut      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]
  non_linear_switch     F         [F] T
  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  on        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
------------------------------------------------------------------------------
Summary of make-definition entities:
    fo8L    q8L     cenjh   odi     qjL     dijL
    fojL    foTL    foHL    qHL
------------------------------------------------------------------------------
** 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
```

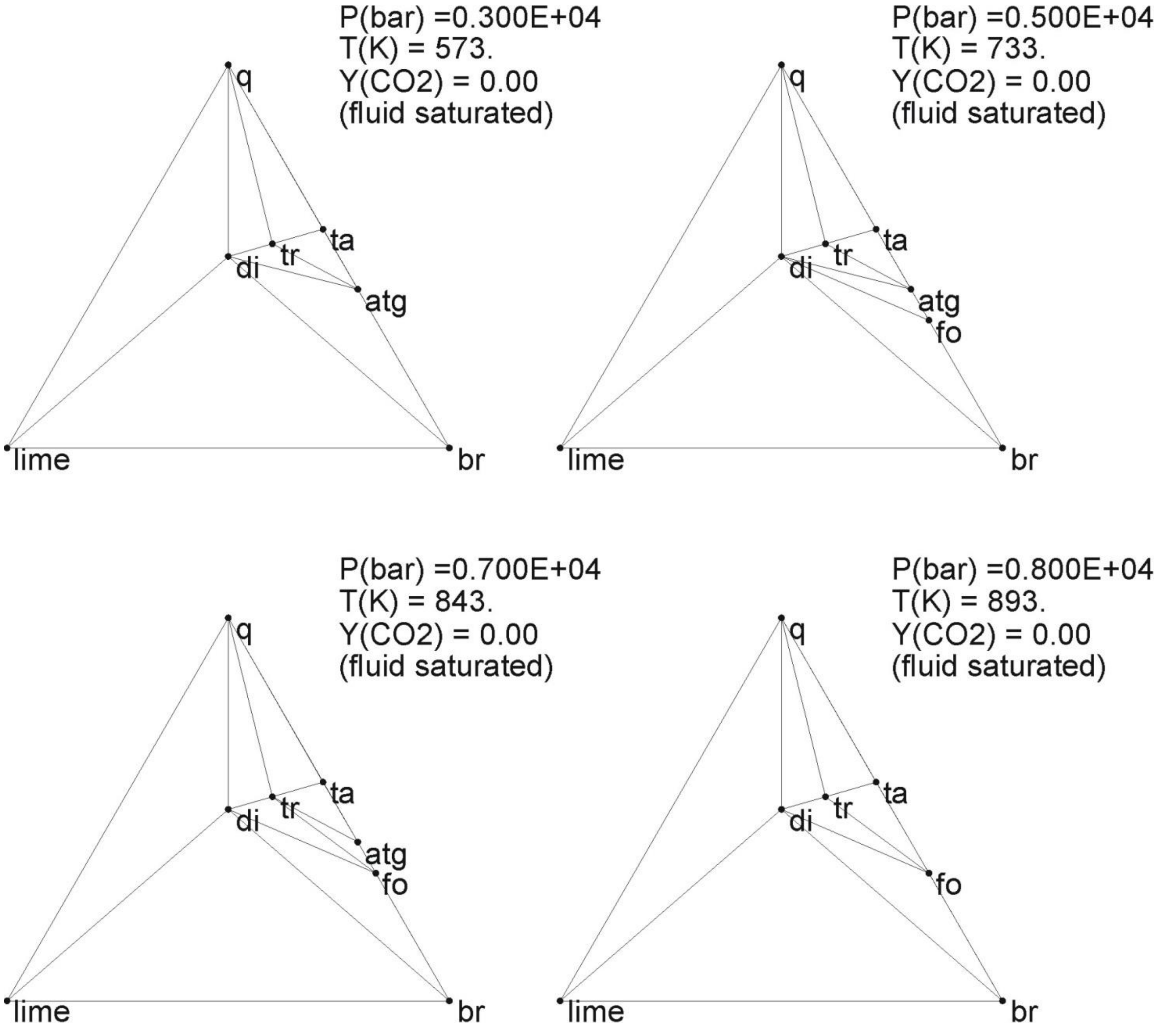
```
cycle        3        4        5
cycle        4        6        7
cycle        5        8        8
Computing the compositional phase relations at condition  9
cycle        1        1        1
cycle        2        2        3
cycle        3        4        5
cycle        4        6        7
cycle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

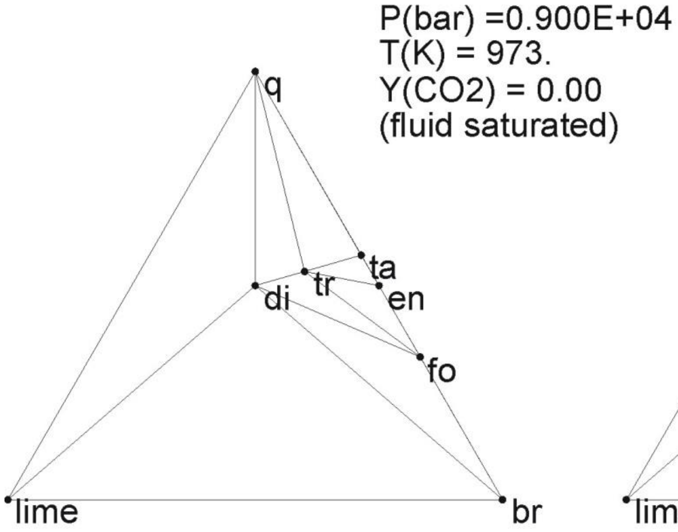
(3) Plotting the calculated phase diagram (PSVDRAW)

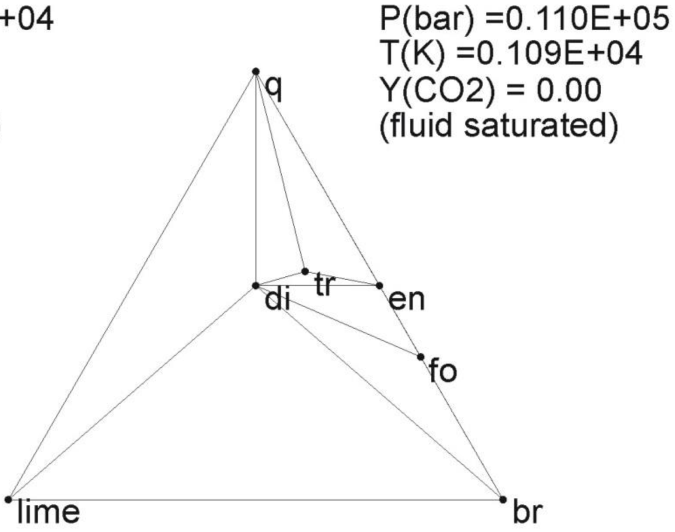
Run PSVDRAW to plot the calculated chemographies:

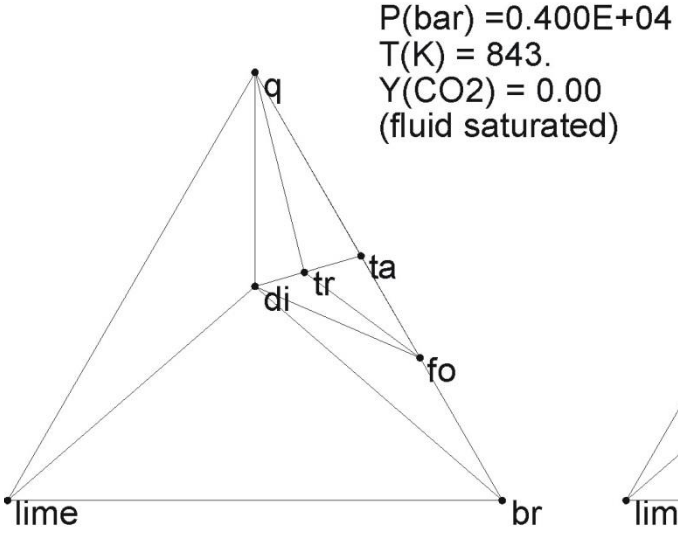
```
C:\PERPLEX\Perplex689>PSVDRAW

Perple_X version 6.8.9, source updated Jan 31, 2020.
Copyright (C) 1986-2002 James A D Connolly <www.perplex.ethz/copyright.html>.

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)
```

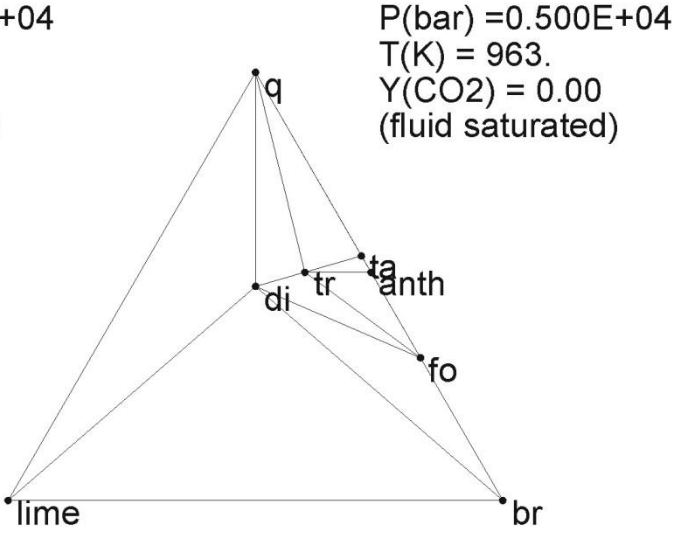
```
To change these options edit or create the plot option file
See: www.perplex.ethz.ch/perplex_plot_options.html

PostScript will be written to file: ex3.ps

Modify the default plot (y/n)?
N
```

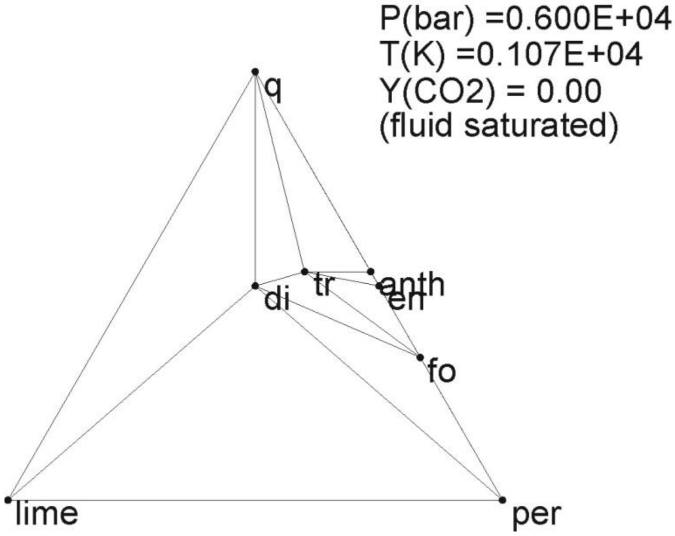



P(bar) =0.900E+04
T(K) = 973.
Y(CO2) = 0.00
(fluid saturated)
q
ta
tr
di
en
fo
lime
br


P(bar) =0.110E+05
T(K) =0.109E+04
Y(CO2) = 0.00
(fluid saturated)
q
tr
di
en
fo
lime
br


P(bar) =0.400E+04
T(K) = 843.
Y(CO2) = 0.00
(fluid saturated)
q
ta
tr
di
fo
lime
br

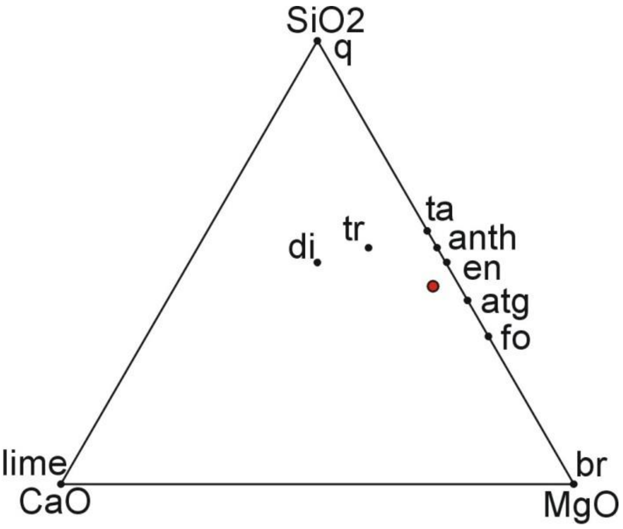

P(bar) =0.500E+04
T(K) = 963.
Y(CO2) = 0.00
(fluid saturated)
q
ta
anth
tr
di
fo
lime
br


P(bar) =0.600E+04
T(K) =0.107E+04
Y(CO2) = 0.00
(fluid saturated)
q
tr
anth
en
di
fo
lime
per

Ex 4

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

This exercise explains how to calculate a very simple pseudosection, not involving solid solutions, for a generic ultramafic composition (MgO=50, SiO_2=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\Perplex689>build

Perple_X version 6.8.9, source updated Jan 31, 2020.
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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  N2 ZnO
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  N2
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 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
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

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 Ex. 2 and Ex. 3.
rnk | rankinite Ca3Si2O7
lrn | larnite Ca2SiO4
cstn | “Si-titanite” CaSi2O5 (one Si replaces Ti)
wo | wollastonite CaSiO3
pswo | pseudo-wollastonite CaSiO3
wal | wollastonite CaSiO3
ak | akermanite Ca2MgSi2O7

```
merw           | merwinite Ca3MgSi2O8
mont           | monticellite CaMgSiO4
chum           | clinohumite Mg9Si4O16(OH)2
cen            | clinoenstatite Mg2Si2O6
cumm           | cummingtonite Mg7Si8O22(OH)2
cumm_dqf       | cummingtonite for Diener et al. (2007) cAmph model
woL            | wollastonite LIQUID
limL           | lime LIQUID
mcpv           | make definitions for Holland et al., 2013 mantle mineralogical model
cmpv           | make definitions for Holland et al., 2013 mantle mineralogical model
cpv            | make definitions for Holland et al., 2013 mantle mineralogical model

Include solution phases (Y/N)?
N

Enter calculation title:
Ex4
```

(2) Doing the calculation (VERTEX)

Run VERTEX to make the calculation:

```
C:\PERPLEX\Perplex689>vertex

Perple_X version 6.8.9, source updated Jan 31, 2020.
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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: hp633ver.dat
Writing print output to file: ex4.plt
Writing plot output to file: ex4.plt
Writing phase assemblage data to file: ex4.blk
Reading solution models from file: not requested
Reading Perple_X options from: perplex_option.dat
Writing seismic data options to: ex4_seismic_data.txt
Writing Perple_X option summary to: not requested

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       5       [aut] or 1->12; aut = automatic
  refinement_switch       F       [T] F
  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]
  non_linear_switch      F         [F] T
  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   on        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       T         [T] F; echo auto-refine compositions
  seismic_data_file      T         [F] T; echo seismic wavespeed options
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
--------------------------------------------------------------------------------
Summary of make-definition entities:
    fo8L      q8L      cenjh     odi      qjL      dijL     fojL      foTL      foHL      qHL
--------------------------------------------------------------------------------
**warning ver099**  no data for aqueous species, aq_output and aq_lagged_speciation disabled.

** 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.
```

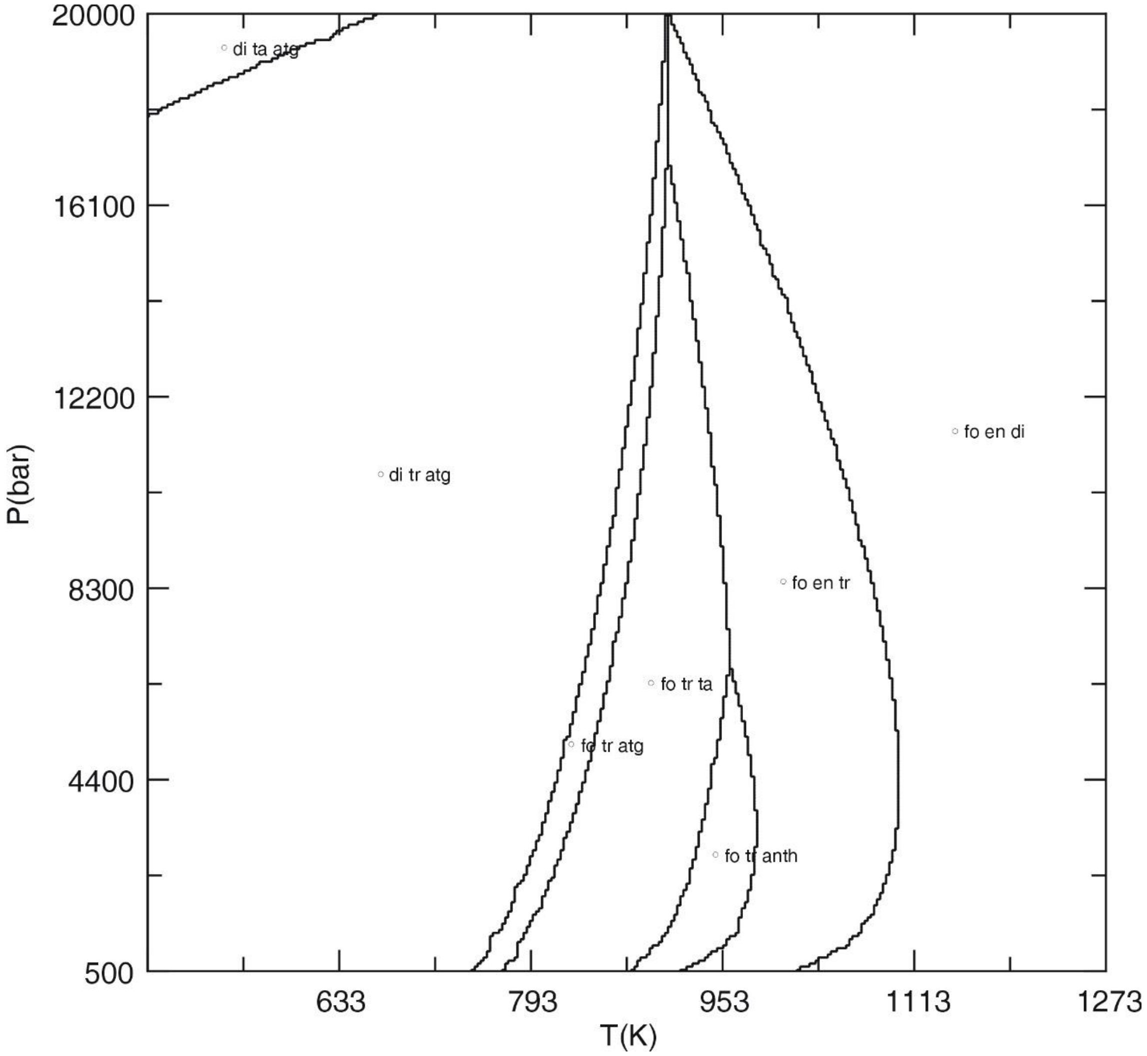
```
 97.4% done with low level grid.
100.0% done with low level grid.

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\Perplex689>pssect

Perple_X version 6.8.9, source updated Jan 31, 2020.
Copyright (C) 1986-2020 James A D Connolly <www.perplex.ethz/copyright.html>.

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)
```

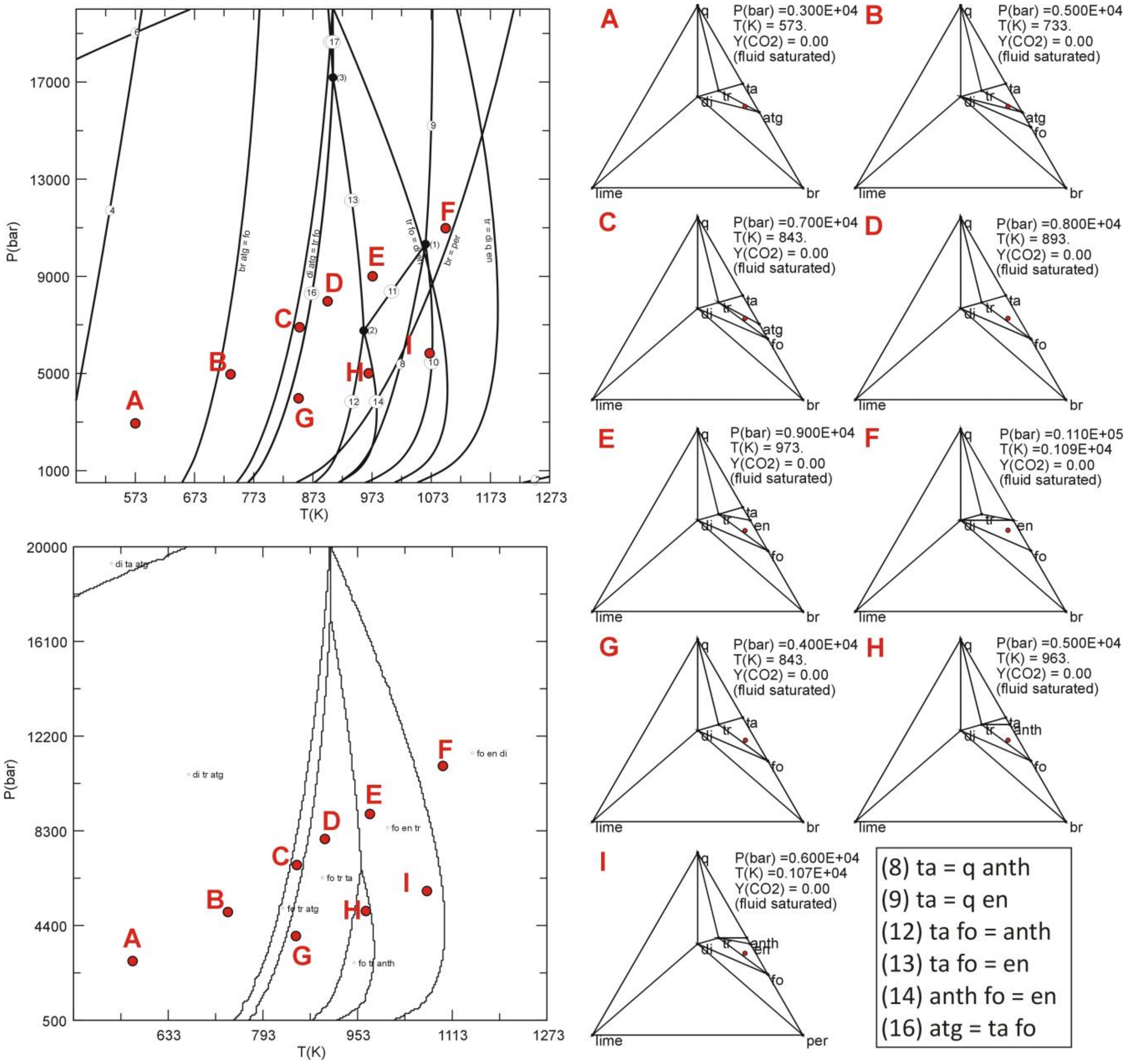
```
                    0.180    [0.18] y-scale (rel)
                     130.    [0.18] x-translation (pts)
                     220.    [0.18] y-translation (pts)
                     0.00    [0.0]  rotation (deg)
  plot_aspect_ratio     1.000     [1.0] x_axis_length/y_axis_length
  replicate_label       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
```



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



(8) ta = q anth
(9) ta = q en
(12) ta fo = anth
(13) ta fo = en
(14) anth fo = en
(16) atg = ta fo

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(CO_2) projections and pseudosections for the CMS-H_2O-CO_2 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(CO_2) projections and T-X(CO_2) pseudosections and allows you to become familiar with the use of H_2O-CO_2 fluids.

Ex. 5.1 – Isobaric T-X(CO_2) projection for a generic siliceous dolomite containing excess Cal

(1) Definition of the problem (BUILD)

```
C:\PERPLEX\Perplex689>build

Perple_X version 6.8.9, source updated Jan 31, 2020.
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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 N2 ZnO
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 N2 ZnO
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 N2 ZnO
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)
0.00001
1
```

CONVEX might not be able to trace equilibria which occur at very low XCO2 values (XCO2 < 1 e-6); therefore, it is suggested to set a XCO2 minim value different from 0 (e.g. 0.00001)

```
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

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:
```

At very low XCO2 values, equilibria involving Ca- and/or Mg-rich silicates such as rankinite, larnite, akermanite, merwinite, spurrite tylleite, monticellite, chlinohumite, clinohumite and clinoenstatite could become metastable, therefore their exclusion is meaningful.

```
rnk          | rankinite Ca3Si2O7
lrn          | larnite Ca2SiO4
cstn         | "Si-titanite" CaSi2O5 (one Si replaces Ti)
ty           | tilleyte Ca5Si2O7(CO3)2
spu          | spurrite Ca5Si2O8(CO3)
ak           | akermanite Ca2MgSi2O7
merw         | merwinite Ca3MgSi2O8
mont         | monticellite CaMgSiO4
chum         | clinohumite Mg9Si4O16(OH)2
cen          | clinoenstatite Mg2Si2O6

Include solution phases (Y/N)?
N

Enter calculation title:
Ex5_1
```

(2) Doing the calculation (CONVEX)

Run CONVEX to make the calculation:

```
C:\PERPLEX\Perplex689>convex

Perple_X version 6.8.9, source updated Jan 31, 2020.
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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: hp633ver.dat
Writing print output to file: ex5_1.plt
Writing plot output to file: ex5_1.plt
Reading solution models from file: not requested
Reading Perple_X options from: perplex_option.dat
Writing complete reaction list to: not requested
Writing Perple_X option summary to: not requested

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]
   non_linear_switch      F         [F] T
   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   on         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
--------------------------------------------------------------------------------
Summary of make-definition entities:
    cumm_dqf  fo8L     q8L      cenjh    odi      qjL     dijL     fojL     foTL     mcpv     cmpv     foHL    qHL
--------------------------------------------------------------------------------
--------------------------------------------------------------------------------
Summary of saturated-component entities:
  for: CaO
    lime     cc       arag     limL
--------------------------------------------------------------------------------
** 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.
**warning ver079** univeq failed on an edge for the following equilibrium.
 Probable cause is extreme independent variable limits (e.g., xco2=0)  or poor convergence criteria in the
thermodynamic data file. In routine:COFACE
finished with equilibrium (     1) dol = br
Testing divariant assemblage      2,      2 assemblages remaining to be tested.
**warning ver079** univeq failed on an edge for the following equilibrium.
 Probable cause is extreme independent variable limits (e.g., xco2=0) or poor convergence criteria in the
thermodynamic data file. In routine:COFACE
finished with equilibrium (     2) tr = atg di
Testing divariant assemblage      3,      3 assemblages remaining to be tested.
finished with equilibrium (     3) q = wo
finished with equilibrium (     4) di = wo fo
**warning ver020** sfol2
finished with equilibrium (     5) di = wo br
**warning ver047** univariant field         6 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 (     6) di br = fo
**warning ver020** sfol2
finished with equilibrium (     6) di br = fo
finished with equilibrium (     7) fo = wo br
Testing divariant assemblage      4,      4 assemblages remaining to be tested.
finished with equilibrium (     8) dol ta = atg
finished with equilibrium (     9) dol tr = atg
finished with equilibrium (    10) ta = atg tr
```

```
finished with equilibrium (   11) ta = dol tr
finished with equilibrium (   12) atg dol = fo
**warning ver047** univariant field      13 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 (   13) atg = tr fo
**warning ver020** sfol2
finished with equilibrium (   13) atg = tr fo
finished with equilibrium (   14) dol tr = fo
finished with equilibrium (   15) dol q = ta
finished with equilibrium (   16) dol q = tr
finished with equilibrium (   17) ta q = tr
finished with equilibrium (    1) dol = br
**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) atg br = fo
**warning ver020** sfol2
finished with equilibrium (   18) atg br = fo
finished with equilibrium (    1) dol = br
finished with equilibrium (   19) tr = dol di
finished with equilibrium (   20) dol di = fo
**warning ver047** univariant field      21 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 (   21) tr = fo di
**warning ver047** univariant field      21 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 (   21) tr = fo di
**warning ver047** univariant field      21 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 (   21) tr = fo di
**warning ver047** univariant field      21 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 (   21) tr = fo di
**warning ver020** sfol2
finished with equilibrium (   21) tr = fo di
finished with equilibrium (   22) dol q = di
finished with equilibrium (   23) tr q = di
**warning ver066** Metastable assemblage into FLIPIT:
   atg     dol
v = 1000.00      873.000     0.267547E-01  0.00000      0.00000
Testing divariant assemblage      5,     4 assemblages remaining to be tested.
Testing divariant assemblage      6,     4 assemblages remaining to be tested.
Testing divariant assemblage      7,     5 assemblages remaining to be tested.
Testing divariant assemblage      8,     4 assemblages remaining to be tested.
Testing divariant assemblage      9,     4 assemblages remaining to be tested.
Testing divariant assemblage     10,     4 assemblages remaining to be tested.
Testing divariant assemblage     11,     4 assemblages remaining to be tested.
**warning ver066** Metastable assemblage into FLIPIT:
   ta      atg
v = 1000.00      573.000     0.782242E-02  0.00000      0.00000
Testing divariant assemblage     12,     3 assemblages remaining to be tested.
Testing divariant assemblage     13,     2 assemblages remaining to be tested.
```

```
finished with equilibrium (    5) di = wo br
Testing divariant assemblage    14,     3 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.
finished with equilibrium (   24) atg = di br
finished with equilibrium (    6) fo = di br
finished with equilibrium (   25) atg = di fo
finished with equilibrium (    2) tr = di atg
finished with equilibrium (   21) tr = di fo
**warning ver074** no new equilibria identified, if degenerate segments have  been skipped increase the computational reliability level.
**warning ver066** Metastable assemblage into FLIPIT:
    di      br
v = 1000.00     873.000     0.100000E-04  0.00000     0.00000
Testing divariant assemblage    17,     5 assemblages remaining to be tested.
Testing divariant assemblage    18,     4 assemblages remaining to be tested.
Testing divariant assemblage    19,     3 assemblages remaining to be tested.
Testing divariant assemblage    20,     4 assemblages remaining to be tested.
Testing divariant assemblage    21,     4 assemblages remaining to be tested.
Testing divariant assemblage    22,     3 assemblages remaining to be tested.
Testing divariant assemblage    23,     2 assemblages remaining to be tested.
Testing divariant assemblage    24,     2 assemblages remaining to be tested.
Testing divariant assemblage    25,     1 assemblages remaining to be tested.
Testing divariant assemblage    26,     0 assemblages remaining to be tested.
------------------------------------------------------------------------------
WARNING!! The stability fields of the following equilibria may
have been entirely or partially skipped in the calculation:
 (     1-1) dol = br
 (     2-1) tr = di atg
------------------------------------------------------------------------------
```

(3) Plotting the calculated phase diagram (PSVDRAW)

Run PSVDRAW to plot the calculated phase diagram:

```
C:\PERPLEX\Perplex689>psvdraw

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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)?
y

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

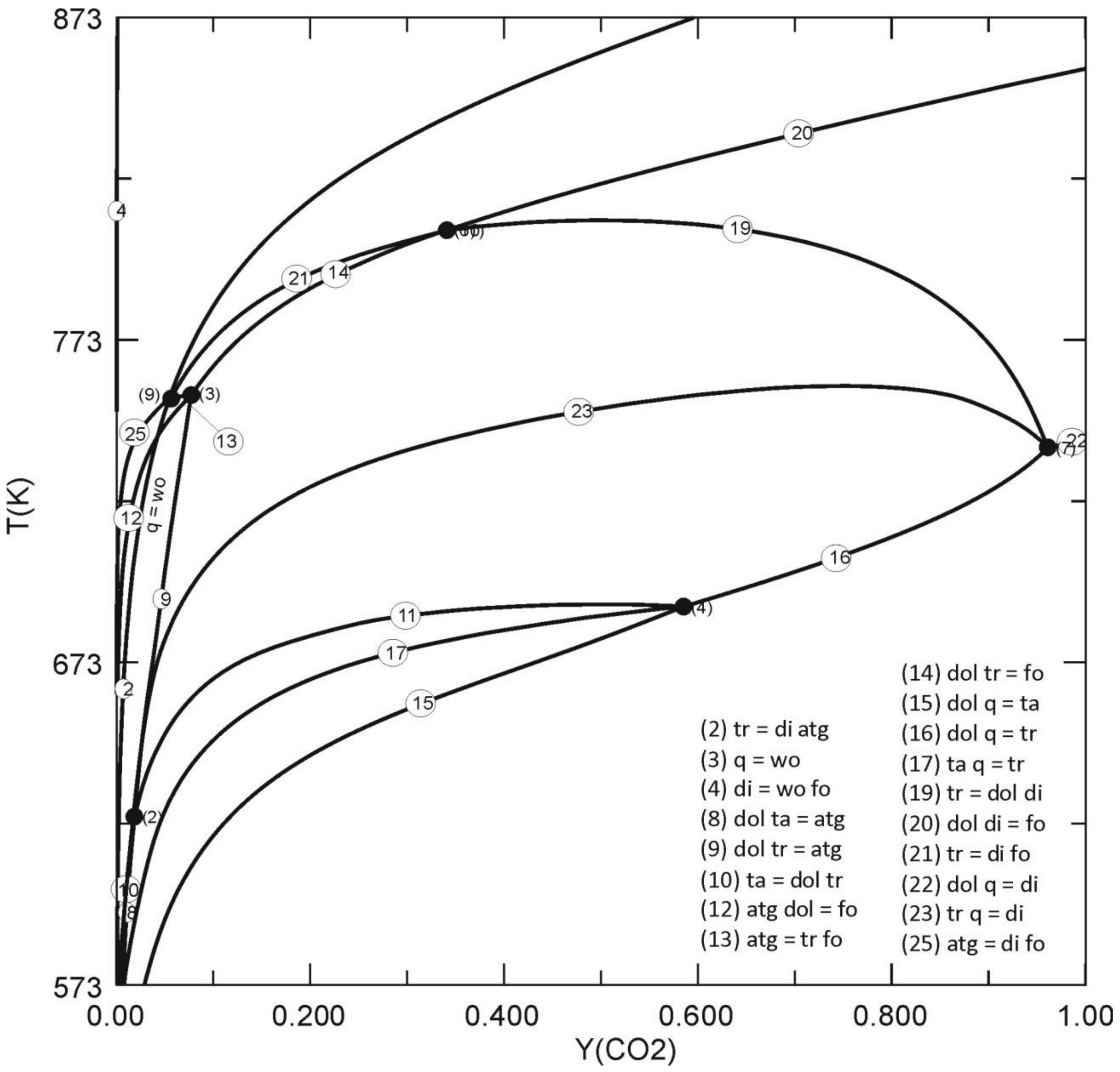
Enter minimum fraction of the axes length that a curve must be to receive a numeric label (0-1.000):
0

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
```



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\Perplex689>build

Perple_X version 6.8.9, source updated Jan 31, 2020.
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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_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 N2 ZnO
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

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   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)
0.00001
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 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 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

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 Ex. 5_1:

```
rnk            | rankinite Ca3Si2O7
lrn            | larnite Ca2SiO4
cstn           | “Si-titanite” CaSi2O5 (one Si replaces Ti)
ty             | tilleyte Ca5Si2O7(CO3)2
spu            | spurrite Ca5Si2O8(CO3)
ak             | akermanite Ca2MgSi2O7
merw           | merwinite Ca3MgSi2O8
mont           | monticellite CaMgSiO4
chum           | clinohumite Mg9Si4O16(OH)2
cen            | clinoenstatite Mg2Si2O6

Include solution models (Y/N)?
n

Enter calculation title:
Ex5_2
```

(2) Doing the calculation (VERTEX)

Run VERTEX to make the calculation:

```
C:\PERPLEX\Perplex689>vertex

Perple_X version 6.8.9, source updated Jan 31, 2020.
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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: hp633ver.dat
Writing print output to file: ex5_2.plt
Writing plot output to file: ex5_2.plt
Writing phase assemblage data to file: ex5_2.blk
Reading solution models from file: not requested
Reading Perple_X options from: perplex_option.dat
Writing seismic data options to: ex5_2_seismic_data.txt
Writing Perple_X option summary to: not requested


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       5       [aut] or 1->12; aut = automatic
  refinement_switch       F       [T] F
  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]
  non_linear_switch      F         [F] T
  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   on        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       T         [T] F; echo auto-refine compositions
  seismic_data_file      T         [F] T; echo seismic wavespeed options
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
--------------------------------------------------------------------------------
Summary of make-definition entities:
   cumm_dqf  fo8L     q8L      cenjh    odi      qjL    dijL     fojL     foTL     mcpv     cmpv     foHL    qHL
--------------------------------------------------------------------------------
**warning ver099**  no data for aqueous species, aq_output and aq_lagged_speciation disabled.
** 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 6.8.9, source updated Jan 31, 2020.
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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)
```
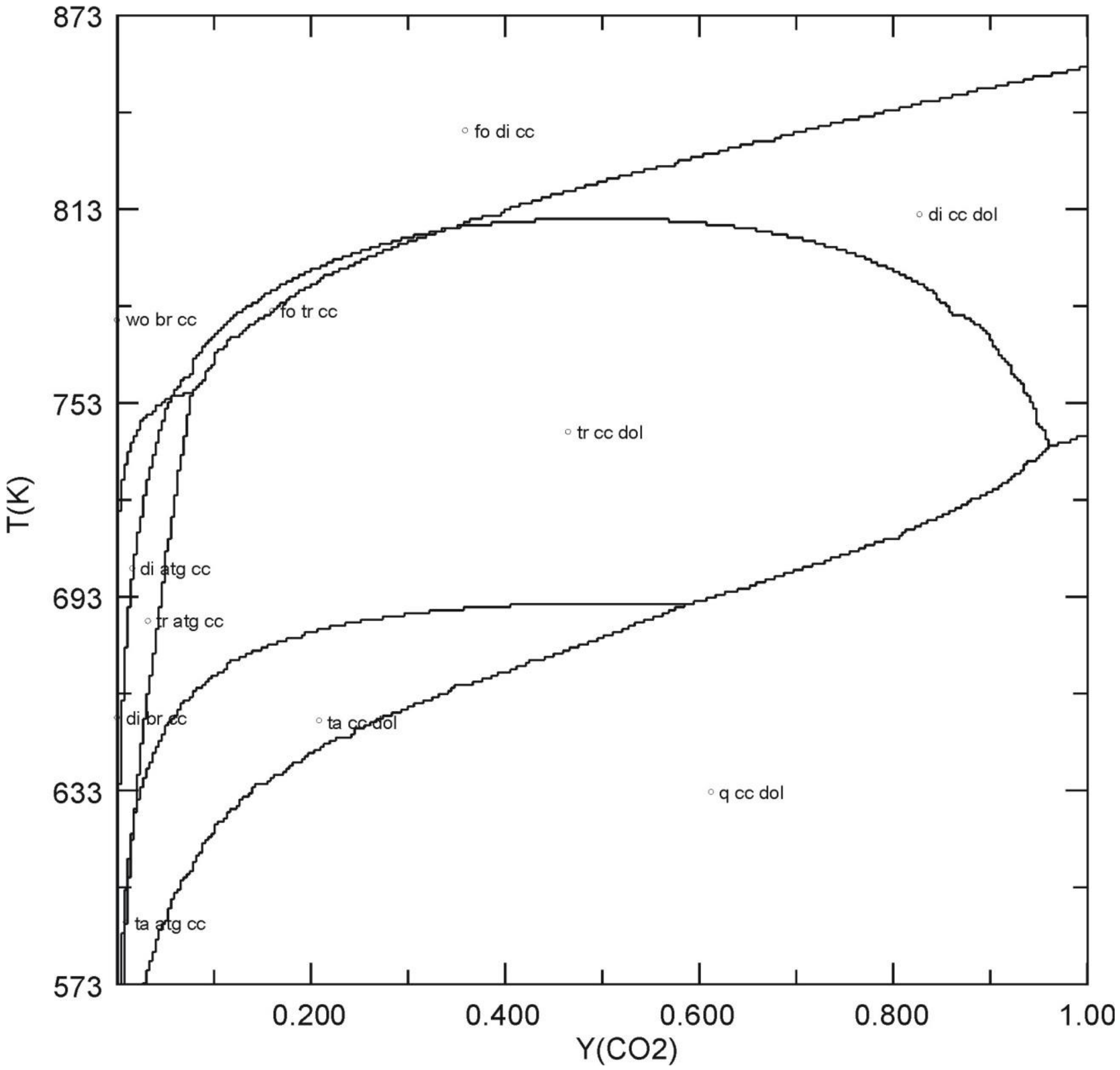
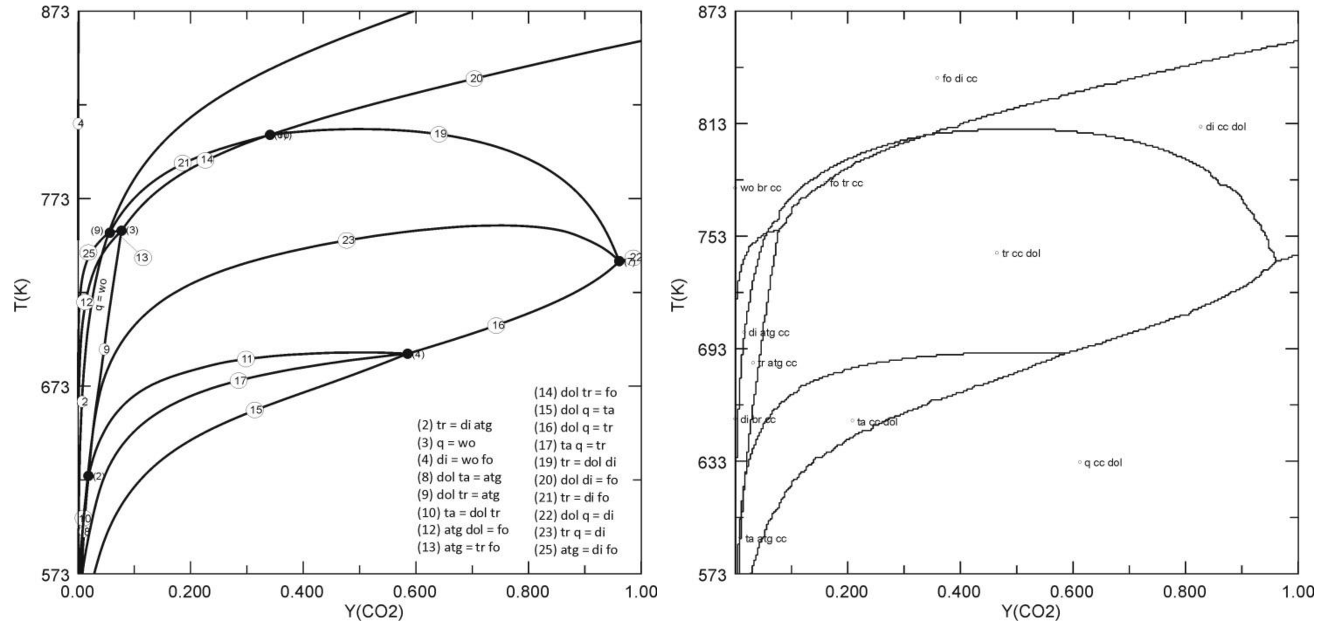

```
                 130.    [0.18] x-translation (pts)
                 220.    [0.18] y-translation (pts)
                 0.00    [0.0]  rotation (deg)
   plot_aspect_ratio     1.000     [1.0] x_axis_length/y_axis_length
   replicate_label       0.250     0->1 [0.025]
   splines               T         [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
```



Comparison between projections and pseudosections



Comparison between the isobaric T-X(CO_2) 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.**

Ex. 5.3 – Isobaric T-X(CO_2) 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 6.8.9, source updated Jan 31, 2020.
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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: hp633ver.dat
Writing print output to file: ex5_3.plt
Writing plot output to file: ex5_3.plt
Reading solution models from file: not requested
Reading Perple_X options from: perplex_option.dat
Writing complete reaction list to: not requested
Writing Perple_X option summary to: not requested

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]
    non_linear_switch      F         [F] T
    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,
    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/speciati
    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   on        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
--------------------------------------------------------------------------------
Summary of make-definition entities:
    cumm_dqf  fo8L     q8L      cenjh    odi      qjL    dijL     fojL     foTL     mcpv     cmpv     foHL     qHL
--------------------------------------------------------------------------------
--------------------------------------------------------------------------------
Summary of saturated-component entities:
  for: SiO2
    q       trd      crst     coe      stv      qL q8L
    q       trd      crst     coe      stv      qL q8L      qjL      qHL
--------------------------------------------------------------------------------
** 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
**warning ver047** univariant field         2 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 (     2) ta dol = tr
**warning ver020** sfol2
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) tr cc = di
**warning ver047** univariant field         6 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 (     6) dol = di
**warning ver020** sfol2
finished with equilibrium (     6) dol = di
finished with equilibrium (     6) dol = di
**warning ver066** Metastable assemblage into FLIPIT:
    ta      tr
v = 1000.00      742.369      1.00000      0.00000      0.00000
Testing divariant assemblage      2,      2 assemblages remaining to be tested.
Testing divariant assemblage      3,      2 assemblages remaining to be tested.
finished with equilibrium (     7) 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.
finished with equilibrium (     8) mag = ta
finished with equilibrium (     2) dol ta = tr
finished with equilibrium (     9) dol mag = tr
finished with equilibrium (     8) mag = ta
finished with equilibrium (    10) mag = en
finished with equilibrium (    11) dol en = tr
finished with equilibrium (    10) mag = en
finished with equilibrium (    12) ta = en
finished with equilibrium (    10) mag = en
finished with equilibrium (     6) dol = di
finished with equilibrium (     6) dol = di
finished with equilibrium (    13) tr = en di
finished with equilibrium (    14) ta = anth
finished with equilibrium (    15) anth = en
**warning ver066** Metastable assemblage into FLIPIT:
    dol      ta
v = 1000.00      873.000      0.742901      0.00000      0.00000
Testing divariant assemblage      9,      2 assemblages remaining to be tested.
Testing divariant assemblage     10,      2 assemblages remaining to be tested.
Testing divariant assemblage     11,      2 assemblages remaining to be tested.
Testing divariant assemblage     12,      2 assemblages remaining to be tested.
```

```
Testing divariant assemblage    13,    2 assemblages remaining to be tested.
Testing divariant assemblage    14,    1 assemblages remaining to be tested.
Testing divariant assemblage    15,    1 assemblages remaining to be tested.
Testing divariant assemblage    16,    0 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,    0 assemblages remaining to be tested.
Testing divariant assemblage    20,    0 assemblages remaining to be tested.
```

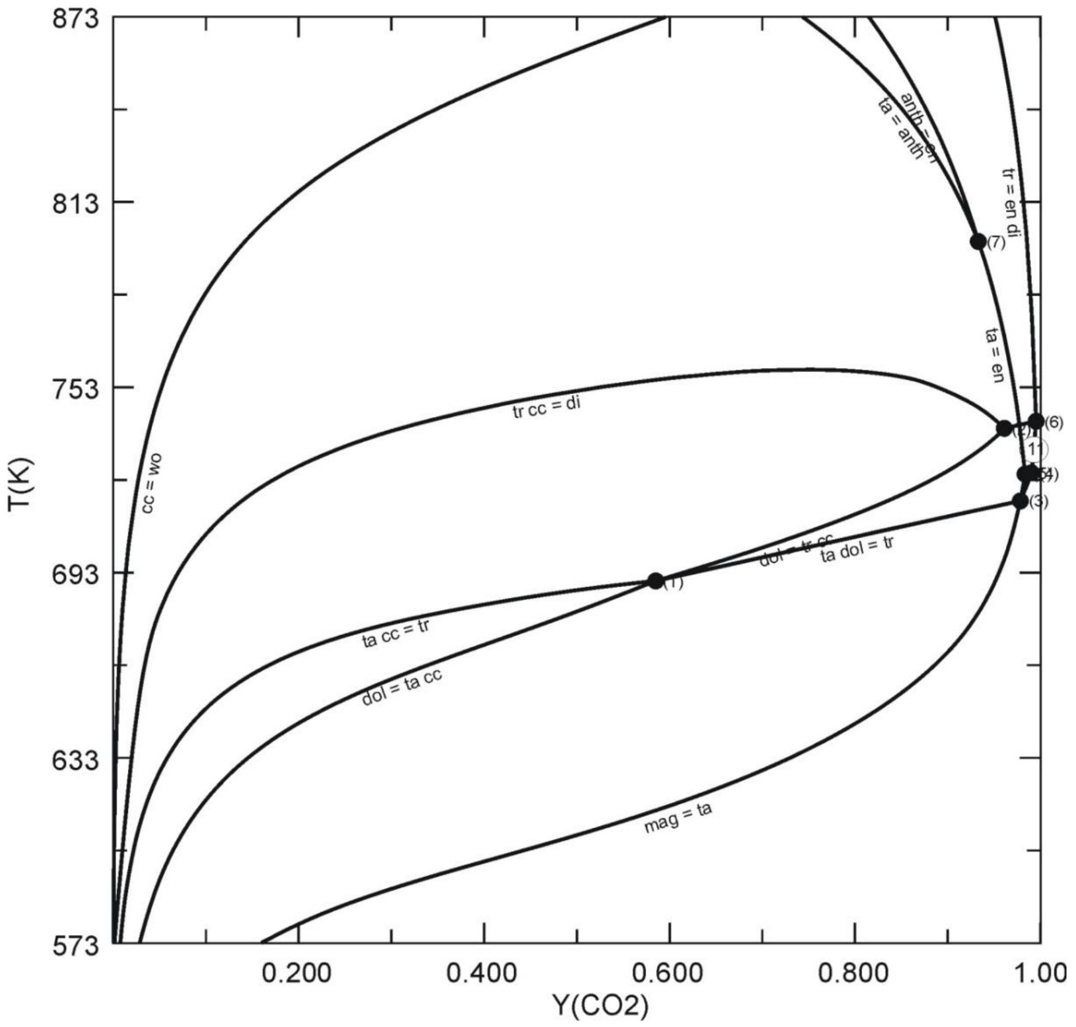
(3) Plotting the calculated phase diagram (PSVDRAW)

Run PSVDRAW to plot the calculated phase diagram:

```
C:\PERPLEX\Perplex689>psvdraw

Perple_X version 6.8.9, source updated Jan 31, 2020.
Copyright (C) 1986-2020 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-XCO₂ 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\Perplex689>vertex

Perple_X version 6.8.9, source updated Jan 31, 2020.
Copyright (C) 1986-2020 James A D Connolly <www.perplex.ethz/copyright.html>.

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: hp633ver.dat
Writing print output to file: ex5_4.plt
Writing plot output to file: ex5_4.plt
Writing phase assemblage data to file: ex5_4.blk
Reading solution models from file: not requested
Reading Perple_X options from: perplex_option.dat
Writing seismic data options to: ex5_4_seismic_data.txt
Writing Perple_X option summary to: not requested

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       5         [aut] or 1->12; aut = automatic
  refinement_switch       F         [T] F
  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]
  non_linear_switch       F         [F] T
  subdivision_override    off       [off] lin str
  hard_limits             off       [off] on
  refine_endmembers       F         [F] T
```

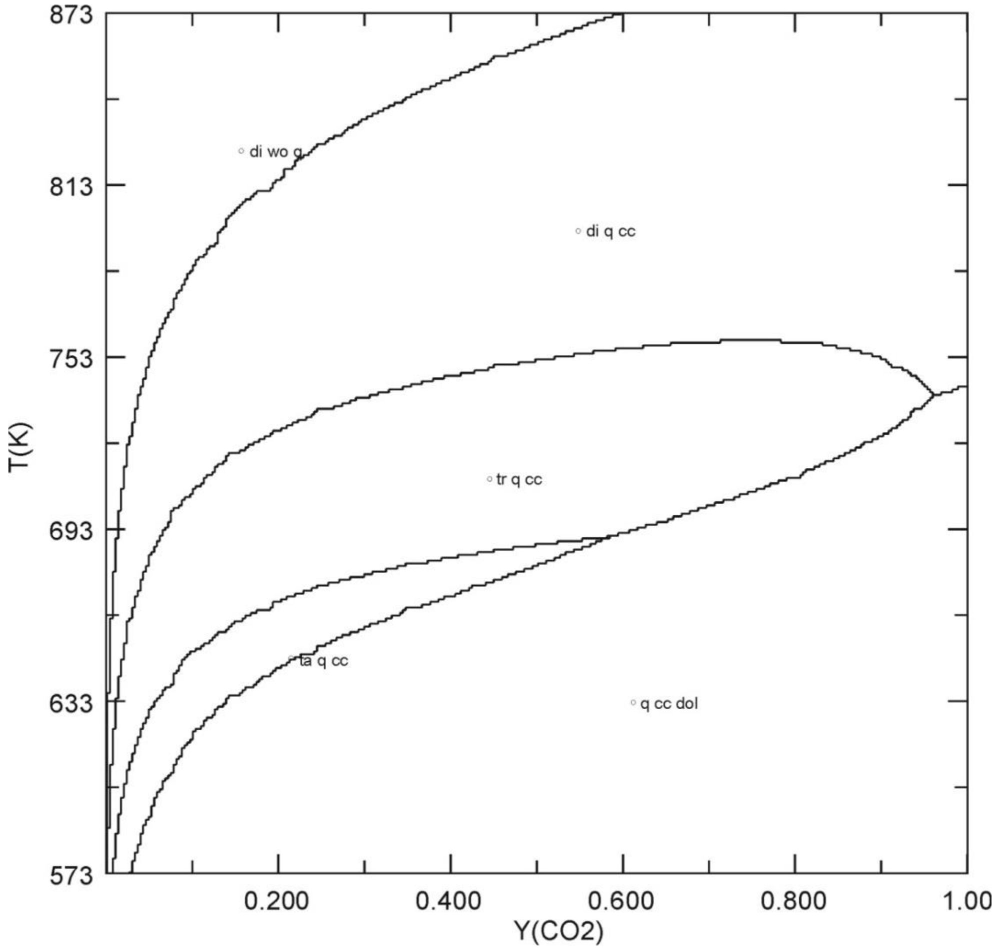
```
  Thermodynamic options:
    solvus_tolerance      aut       [aut] or 0->1; aut = automatic, 0 => p=c pseudocompounds, 1 => homogenize
    T_stop (K)            0.0     [0]
    T_melt (K)          873.0     [873]
    order_check           on        off [on]
    approx_alpha          T         [T] 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   on        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      T         [T] F; echo auto-refine compositions
    seismic_data_file     T         [F] T; echo seismic wavespeed options
  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
--------------------------------------------------------------------------------
Summary of make-definition entities:
    cumm_dqf  fo8L     q8L      cenjh    odi      qjL     dijL     fojL     foTL     mcpv     cmpv     foHL     qHL
--------------------------------------------------------------------------------
**warning ver099**  no data for aqueous species, aq_output and aq_lagged_speciation disabled.
** 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
```

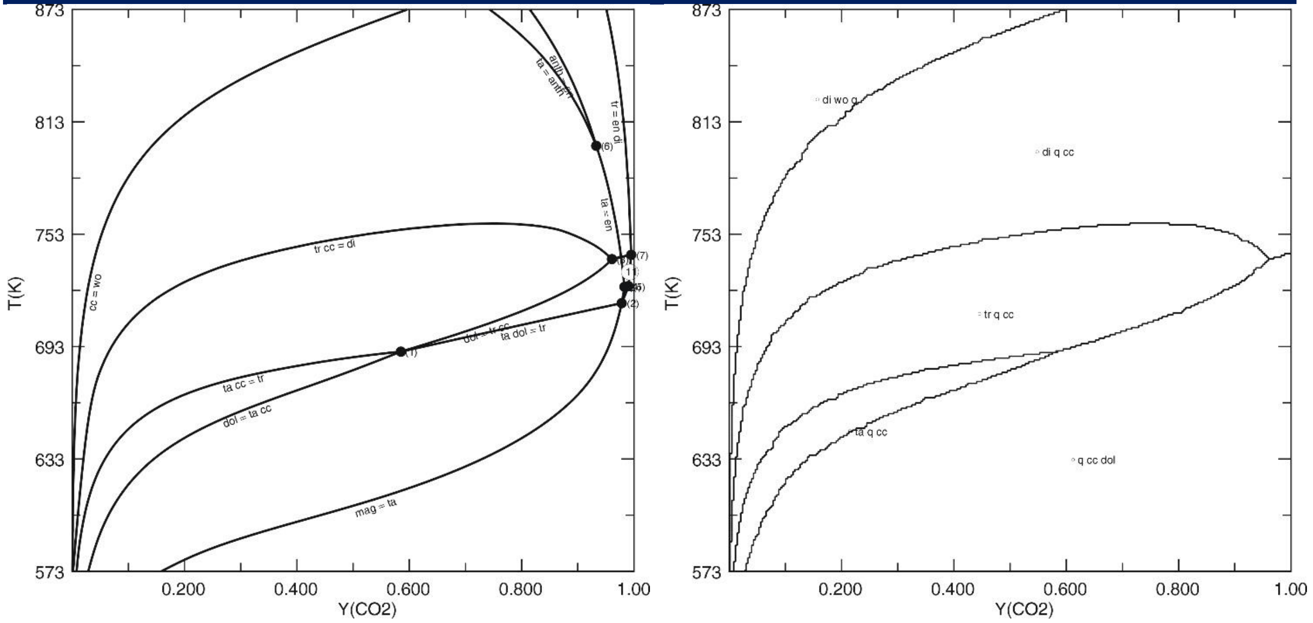
(3) Plotting the calculated phase diagram (PSSECT)

Run PSSECT to plot the calculated pseudosection:

```
C:\PERPLEX\Perplex689>pssect

Perple_X version 6.8.9, source updated Jan 31, 2020.
Copyright (C) 1986-2020 James A D Connolly <www.perplex.ethz/copyright.html>.

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 projections and pseudosections



Comparison between the isobaric T-X(CO2) projection for a generic siliceous limestone containing excess quartz (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 $CaCO_3$-$MgCO_3$ 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, SOLID SOLUTIONS MUST NOW BE CONSIDERED. 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\Perplex689>build

Perple_X version 6.8.9, source updated Jan 31, 2020.
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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]:
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 N2 ZnO
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 N2 ZnO
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

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
4

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

Enter minimum and maximum values, respectively, for: T(K)
573
1273
```

```
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

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
carbonate models:     Do(AE)   Cc(AE)   oCcM(HP)  Carb(M)   oCcM(EF)                dis(EF)
fluid models:        COH-Fluid  COH-Fluid+
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\Perplex689>vertex

Perple_X version 6.8.9, source updated Jan 31, 2020.
Copyright (C) 1986-20209 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: hp633ver.dat
Writing print output to file: ex6_5kbar.plt
Writing plot output to file: ex6_5kbar.plt
Writing phase assemblage data to file: ex6_5kbar.blk
Reading solution models from file: solution_model.dat
Reading Perple_X options from: perplex_option.dat
Writing auto refine summary to: ex6_5kbar_auto_refine.txt
```

```
Writing seismic data options to: ex6_5kbar_seismic_data.txt
Writing pseudocompound glossary to: ex6_5kbar_pseudocompound_glossary.txt
Writing Perple_X option summary to: not requested

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        4        [aut] or 1->12; aut = automatic
   refinement_switch        F        [T] F
   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]
 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]
   non_linear_switch       F         [F] T
   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  on        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      T        [T] F; echo auto-refine compositions
  seismic_data_file     T        [F] T; echo seismic wavespeed options
 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 ver099**  no data for aqueous species, aq_output and aq_lagged_speciation disabled.
------------------------------------------------------------------------------
Solution model summary:
**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

Summary of included solution models:
Do(AE)   Cc(AE)
------------------------------------------------------------------------------
```

This section shows 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
    mag           0.43750      0.51562

Endmember fractions for model: Cc(AE)
    Endmember    Minimum      Maximum
    mag           0.15625E-01     1.0000
```

```
    cc        0.0000       1.0000
--------------------------------------------------------------------------------
Solution model summary:
      6 pseudocompounds generated for: Do(AE)
     47 pseudocompounds generated for: Cc(AE)
Total number of pseudocompounds:      53

Summary of included solution models:
Do(AE)    Cc(AE)
```

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
   633 grid cells to be refined at grid level 4
       ...working (    17 minimizations done)
       ...working (   518 minimizations done)
       ...working (  1019 minimizations done)
       refinement at level 4 involved   1236 minimizations
  3821 minimizations required of the theoretical limit of   98596

Endmember fractions for model: Do(AE)
     Endmember     Minimum        Maximum
     cc          0.48264       0.56424
     mag           0.43576       0.51736

Endmember fractions for model: Cc(AE)
     Endmember     Minimum        Maximum
     mag          0.0000         1.0000
     cc          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\Perplex689>pssect

Perple_X version 6.8.9, source updated Jan 31, 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

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)
```

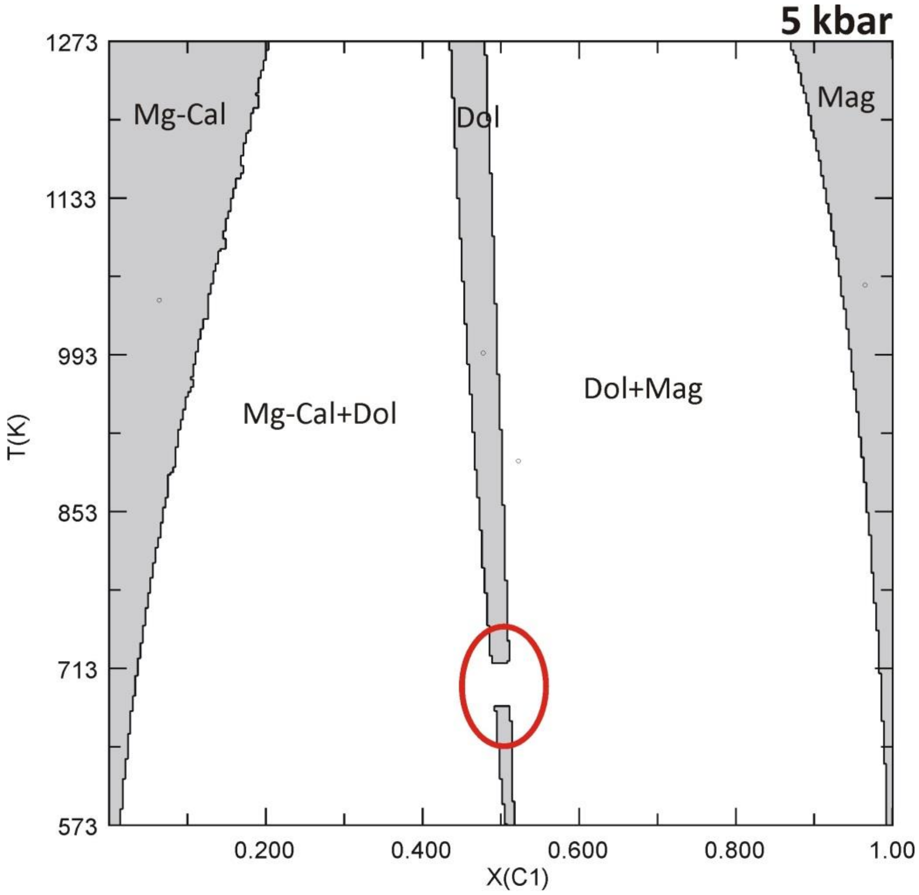
```
   field_fill           T        [T] F
   field_label          T        [T] F
   field_label_scale     0.75      [0.72] (rel)
   font                 Helvetica
   grid                F        [F] T
   half_ticks           T        [T] F
   line_width           1.00      0-99 [1.] (pts)
   picture_transformation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

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.

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

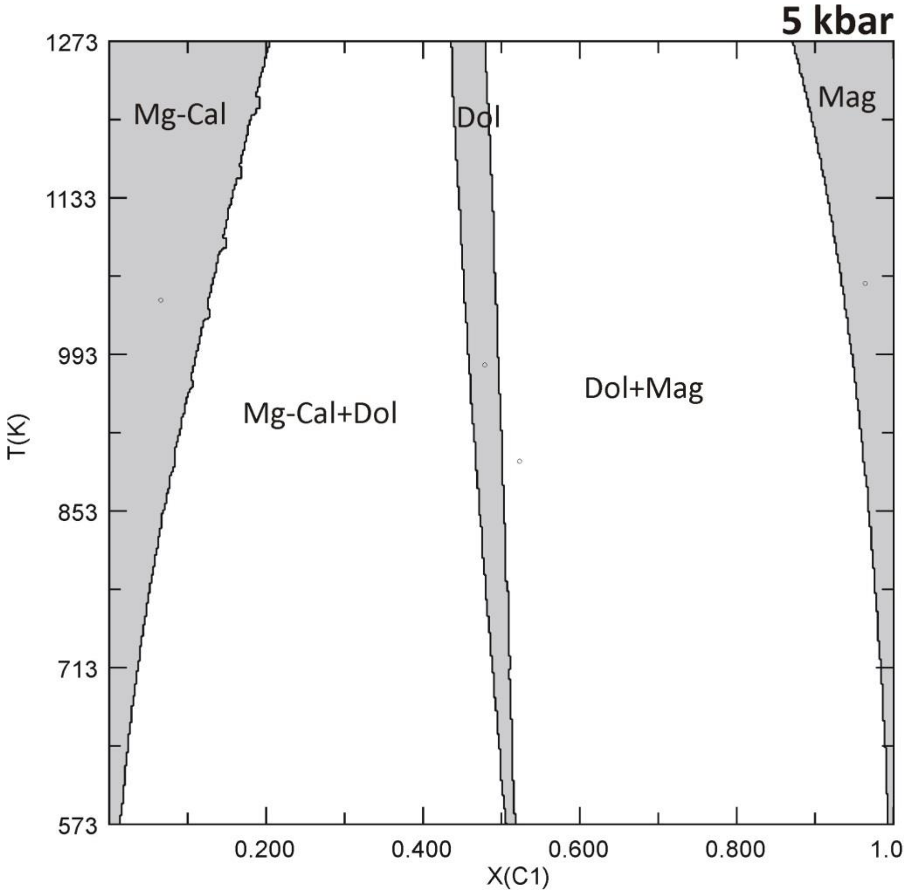
(4) Increasing the resolution of the x-y grid

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.

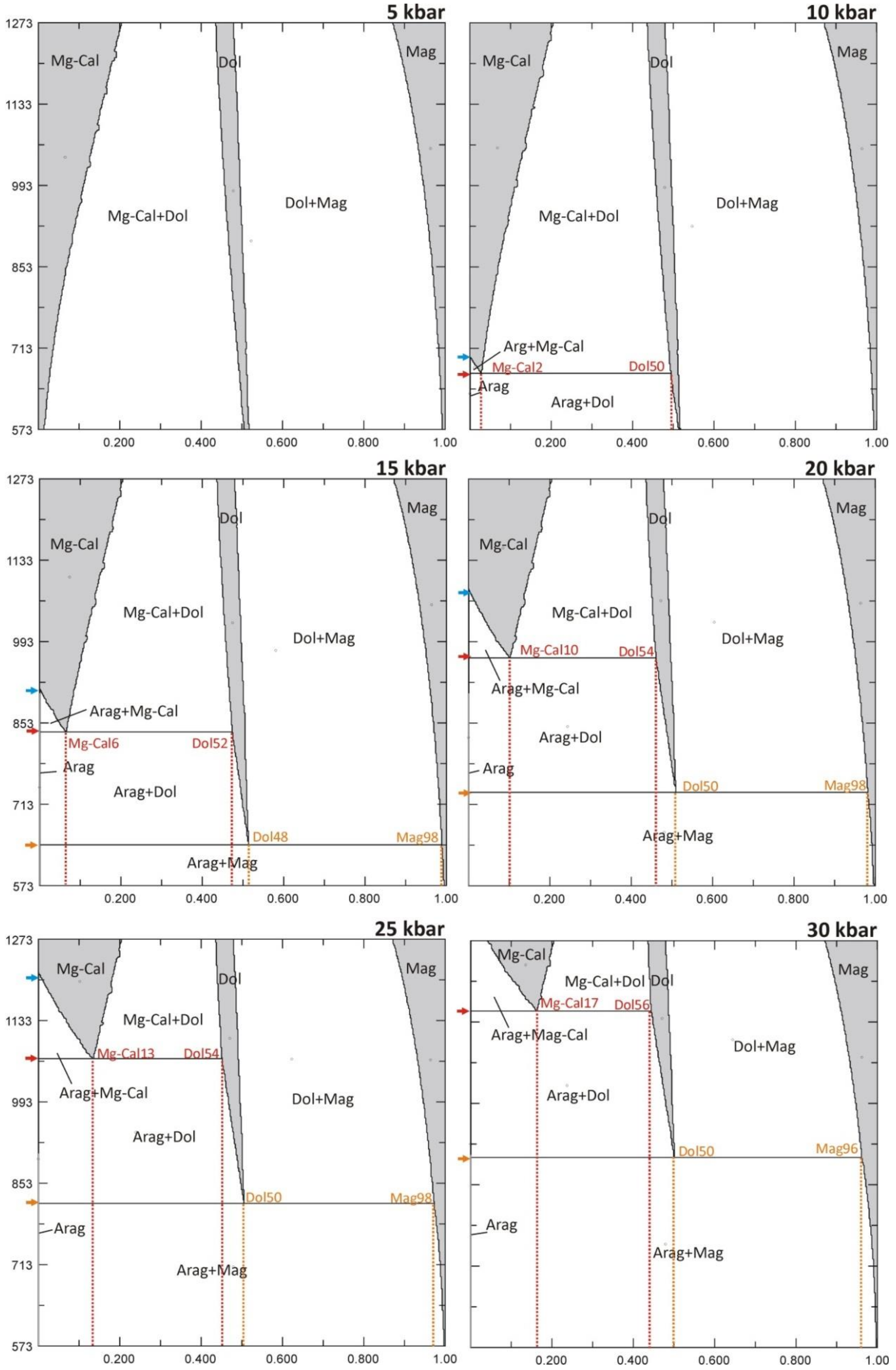


(5) Exploring the influence of pressure on the Cal-Dol and Dol-Mag *solvi*

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 $CaCO_3$-$MgCO_3$ system using solid solutions

This exercise explains how to calculate a P-T projection for the $CaCO_3$-$MgCO_3$ 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\Perplex689>build

Perple_X version 6.8.9, source updated Jan 31, 2020.
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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 N2 ZnO
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 N2 ZnO
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
carbonate models:      Do(AE)    Cc(AE)    oCcM(HP)   Carb(M)    oCcM(EF)                    dis(EF)
fluid models:          COH-Fluid  COH-Fluid+
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\Perplex689>convex

Perple_X version 6.8.9, source updated Jan 31, 2020.
Copyright (C) 1986-2020 James A D Connolly <www.perplex.ethz/copyright.html>.

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: hp633ver.dat
Writing print output to file: ex7.plt
Writing plot output to file: ex7.plt
Reading solution models from file: solution_model.dat
Reading Perple_X options from: perplex_option.dat
Writing complete reaction list to: not requested
Writing auto refine summary to: ex7_auto_refine.txt
Writing pseudocompound glossary to: not requested
Writing Perple_X option summary to: not requested

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]
  non_linear_switch      F         [F] T
  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   on        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
--------------------------------------------------------------------------------
Solution model summary:
**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

Summary of included solution models:
Do(AE)    Cc(AE)
--------------------------------------------------------------------------------
** 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
    mag         0.43750        0.50000

Endmember fractions for model: Cc(AE)
    Endmember     Minimum        Maximum
    mag         0.62500E-01    0.93750
    cc          0.62500E-01    0.93750
-------------------------------------------------------------------------------
Solution model summary:
     10 pseudocompounds generated for: Do(AE)
     47 pseudocompounds generated for: Cc(AE)
Total number of pseudocompounds:      57

Summary of included solution models:
Do(AE)    Cc(AE)
-------------------------------------------------------------------------------
** 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
    mag          0.43750       0.52083

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

(3) Plotting the calculated phase diagram (PSVDRAW)

Run PSWDRAW to plot the calculated pseudosection:

```
C:\PERPLEX\Perplex689>psvdraw

Perple_X version 6.8.9, source updated Jan 31, 2020.
Copyright (C) 1986-2020 James A D Connolly <www.perplex.ethz/copyright.html>.

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 file
See: 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.

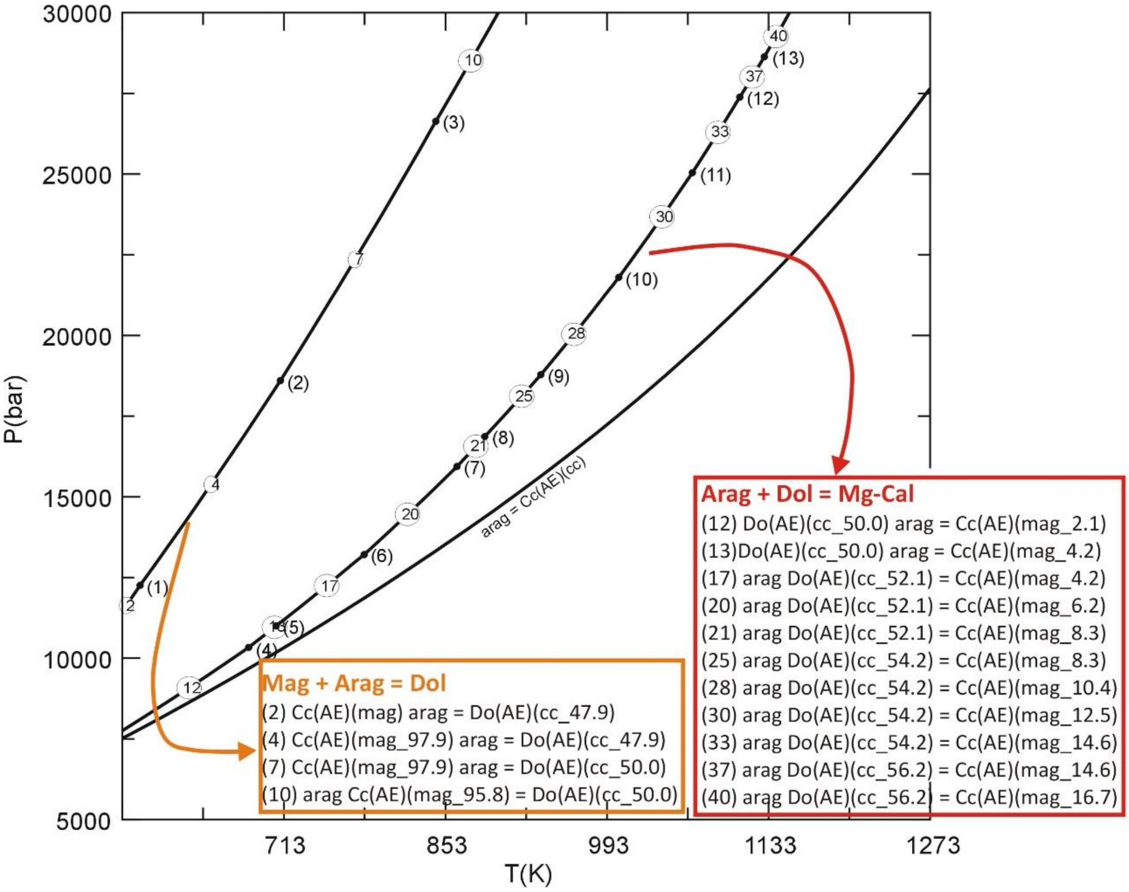
0

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)

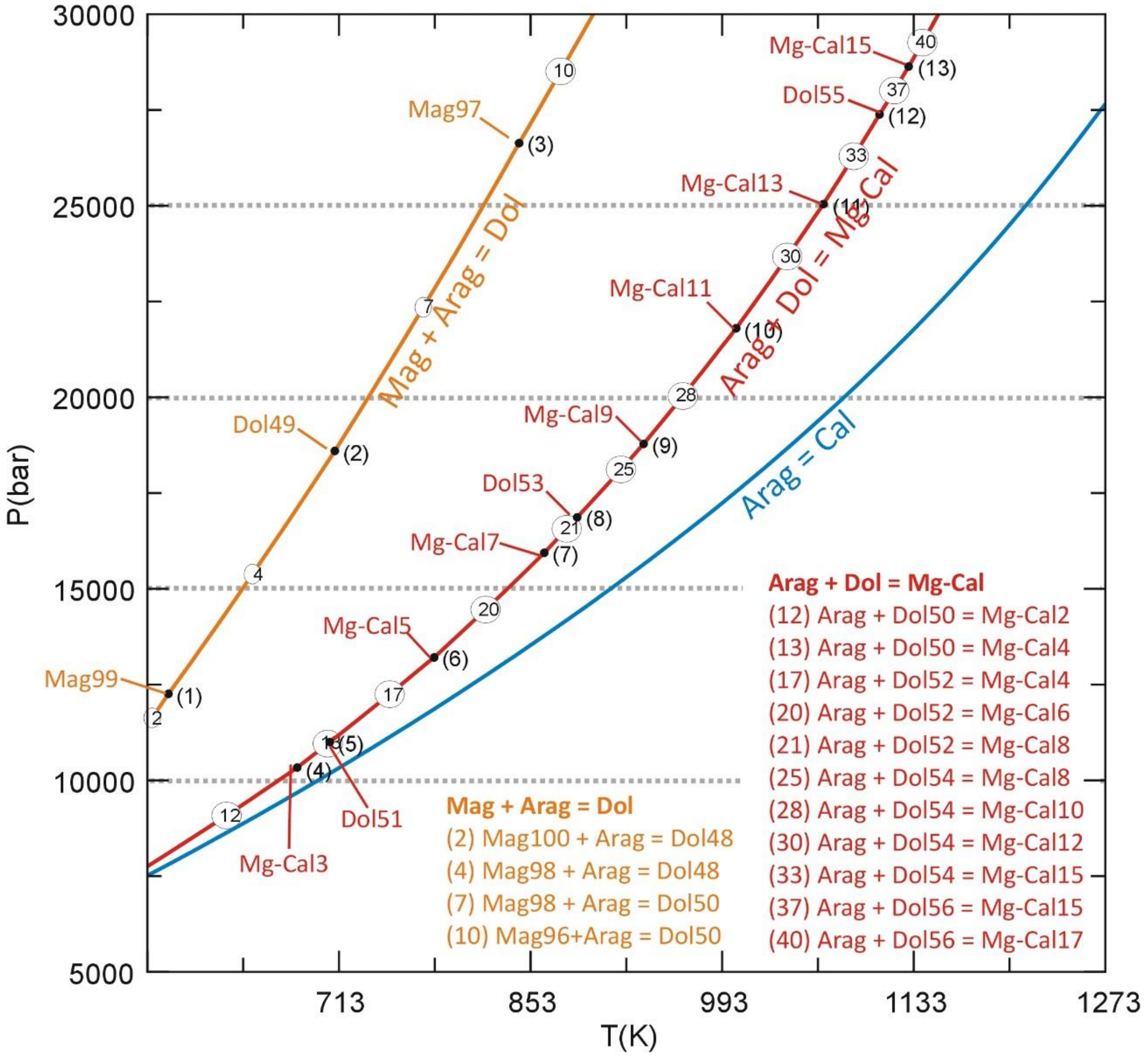
Arag + Dol = Mg-Cal

(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

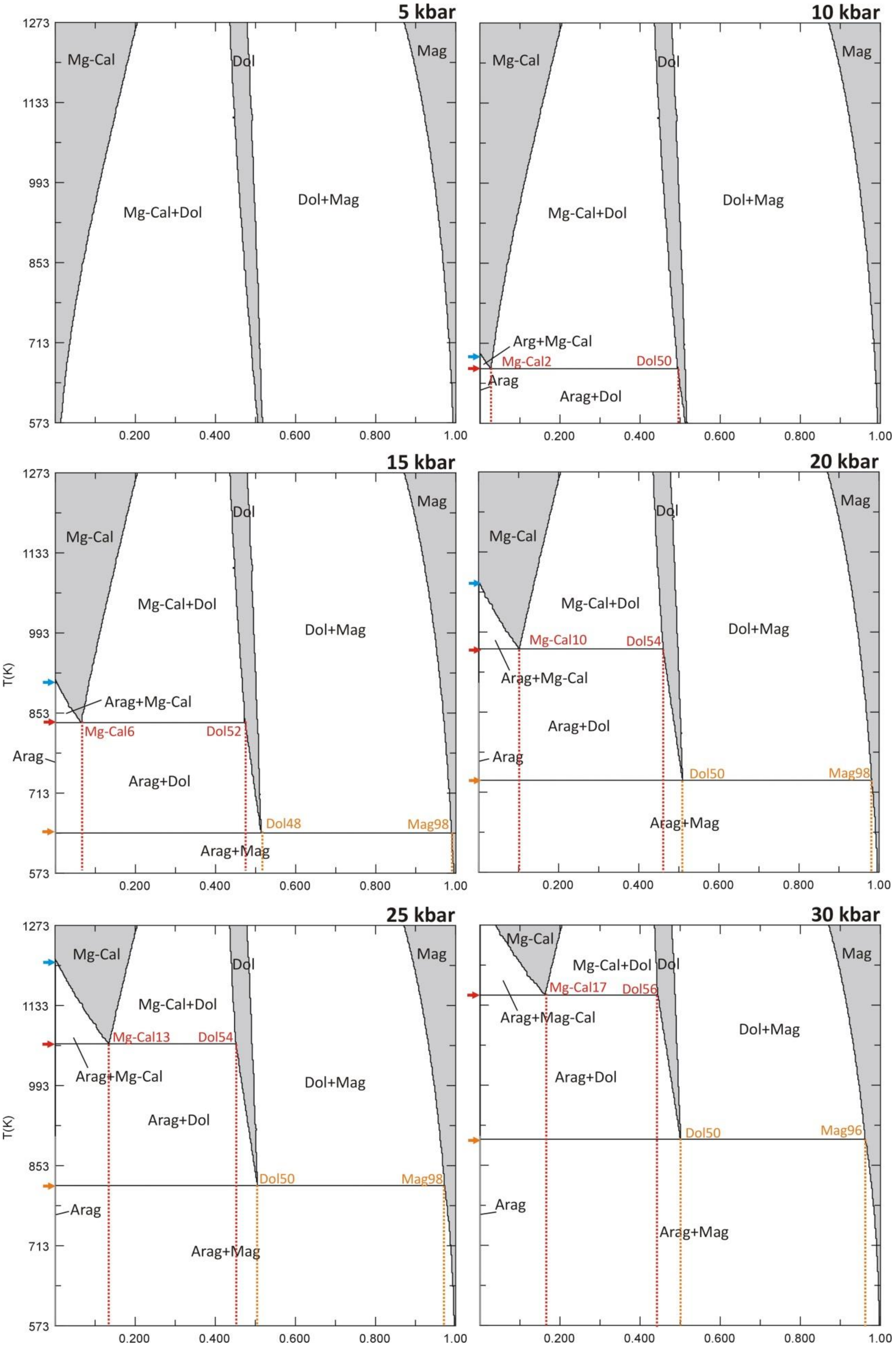
You can now compare the P-T projection with the T-XMgO sections obtained in Ex. 6.



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.


5 kbar
10 kbar
15 kbar
20 kbar
25 kbar
30 kbar
T(K)
1273
1133
993
853
713
573
0.200
0.400
0.600
0.800
1.00
Mg-Cal
Dol
Mag
Mg-Cal+Dol
Dol+Mag
Arg+Mg-Cal
Mg-Cal2
Dol50
Arag
Arag+Dol
Arag+Mg-Cal
Mg-Cal6
Dol52
Dol48
Mag98
Arag+Mag
Mg-Cal10
Dol54
Dol50
Mag98
Mg-Cal13
Dol54
Dol50
Mag98
Mg-Cal17
Dol56
Arag+Mag-Cal
Dol50
Mag96

Ex 8

Ex. 8 – AFM chemographies in the KFMASH system

This exercise explains how to calculate the “classical” Thompson AFM diagrams for metapelites in the KFMASH system. Opposite to Ex. 3, solid solutions are considered.

COMPONENT TRANSFORMATIONS are necessary in order to compute these phase diagrams. In the classical AFM projection, compositions are reduced through the projection hierarchy H2O, SiO2 (q), KAl3O5 (mu) into the sub-composition MgO-FeO-Al2O3.

(1) Projection through muscovite implies that **a muscovite component must be defined (MU = 0.5 K2O + 1.5 Al2O3)**. Along the KAl3O5-SiO2 join, K-feldspar has a negative composition and it will be therefore rejected. This means that **the calculation will only be valid within the stability field for Mu + Qz**.

(2) Projecting from muscovite into the AFM space, biotite has a negative composition and would be excluded by CONVEX. This problem is circumvented by defining two components, **PHL (= 1.5 MgO – 0.5Al2O3)** and **ANN (= 1.5 FeO – 0.5Al2O3)**, to replace the normal FeO and MgO components, so that biotite plots inside the composition space considered by CONVEX.

(1) Definition of the problem (BUILD)

```
C:\PERPLEX\Perplex689>build

Perple_X version 6.8.9, source updated Jan 30, 2020.
Copyright (C) 1986-2020 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

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 N2 ZnO
Transform them (Y/N)?
y
```

Three new components should be defined here:

MU = 0.5 K2O + 1.5 Al2O3

PHL = 3 MgO - Al2O3

ANN (=3 FeO - Al2O3)

MU will be defined by replacing the normal K2O component, whereas PHL and ANN are defined by replacing the normal MgO and FeO components.

```
Enter new component name, < 6 characters, left justified:
MU
Enter old component to be replaced with MU   :
K2O
Enter other components (< 11) in MU    1 per line, <enter> to finish:
Al2O3

Enter stoichiometric coefficients of:
  K2O   Al2O3
in MU    (in above order):
```

Muscovite has the formula: KAl3Si3O10(OH)2; if SiO2 and H2O are considered in excess, its composition is defined by 0.5 K2O + 1.5 Al2O3 (KAl3O5)

```
0.5
1.5
 MU    =   0.50 K2O    1.50 Al2O3
Is this correct (Y/N)?
y

The current data base components are:
Na2O MgO  Al2O3 SiO2 MU  CaO  TiO2  MnO  FeO  NiO   ZrO2  Cl2 O2  H2O  CO2  CuO  Cr2O3 S2  F2  N2 ZnO
Transform them (Y/N)?
```

Note that the newly defined MU component has replaced K2O in the list of the database components.

```
Y

Enter new component name, < 6 characters, left justified:
PHL
Enter old component to be replaced with PHL  :
MgO
Enter other components (< 11) in PHL   1 per line, <enter> to finish:
Al2O3

Enter stoichiometric coefficients of:
  MgO   Al2O3
in PHL   (in above order):
```

Phlogopite has the formula: KMg3AlSi3O10(OH)2. Considering H2O, SiO2 and KAl3O5 in excess, its composition is defined as PHL = (3MgO – Al2O3) or, reduced, PHL = (1.5MgO – 0.5Al2O3).

```
1.5
```

```
-0.5
 PHL  =  1.50 MgO  -0.50 Al2O3
Is this correct (Y/N)?
Y

The current data base components are:
Na2O  PHL  Al2O3 SiO2  MU  CaO  TiO2  MnO   FeO   NiO  ZrO2  Cl2  O2  H2O CO2 CuO  Cr2O3 S2  F2  N2 ZnO
Transform them (Y/N)?
```

Note that the newly defined PHL component has replaced MgO in the list of the database components.

```
y
Enter new component name, < 6 characters, left justified:
ANN
Enter old component to be replaced with ANN  :
FeO
Enter other components (< 11) in ANN   1 per line, <enter> to finish:
Al2O3

Enter stoichiometric coefficients of:
  FeO   Al2O3
in ANN   (in above order):
```

Annite has the formula: KFe3AlSi3O10(OH)2. Considering H2O, SiO2 and KAl3O5 in excess, its composition is defined as ANN = (3FeO – Al2O3) or, reduced, ANN = (1.5FeO – 0.5Al2O3).

```
1.5
-0.5
 ANN  =  1.50 FeO  -0.50 Al2O3
Is this correct (Y/N)?
y

The current data base components are:
 Na2O  PHL  Al2O3 SiO2 MU  CaO  TiO2  MnO  ANN   NiO  ZrO2  Cl2 O2  H2O CO2  CuO  Cr2O3 S2  F2  N2 ZnO
Transform them (Y/N)?
```

Note that the newly defined ANN component has replaced FeO in the list of the database components.

```
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.
H2O

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

SiO2 and MU (KAl3O5) must be considered as saturated component, in this specific order.

```
Select < 6 saturated components from the set:
Na2O  PHL  Al2O3 SiO2  MU  CaO  TiO2  MnO  ANN  NiO  ZrO2  Cl2  O2   CO2  CuO  Cr2O3 S2   F2   N2 ZnO
Enter names, 1 per line, press <enter> to finish:
SiO2
MU

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

Select thermodynamic components from the set:
Na2O  PHL  Al2O3 CaO  TiO2  MnO  ANN  NiO  ZrO2  Cl2  O2   CO2 CuO  Cr2O3 S2   F2   N2 ZnO
Enter names, 1 per line, press <enter> to finish:
ANN
PHL
Al2O3
```

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: 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
0

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:
Exclude K-bearing phases other than muscovite and biotite.
fstp       |Fe-stilpnomelane
mstp       |Mg-stilpnomelane
cel        | celadonite  KMgAlSi4O10(OH)2
fcel       | Fe-celadonite  KFeAlSi4O10(OH)2
kcm        | K-cymrite  KAlSi3O8 · H2O
wa         | wadeleite K2Si4O9
hol        | hollandite KAlSi3O8
kls        | kalsilite KAlSiO4
lc         | leucite KAlSi2O6
kjdh       | make-definition for Holland et al., 2018 Cpx solution model
kjL        | make-definition for Holland et al., 2018 melt solution model
kspL       | K-feldspar liquid
lcL        | leucite liquid
```

```
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
biotite models:         Bio(TCC)   Bi(W)      Bi(HGP)    Bio(WPH)   Bio(HP)
clinoamphibole models:   cAmph(G)   Cumm       cAmph(DP)
clinopyroxene models:    Cpx(HGP)   Augite(G)  Cpx(JH)
…
…
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)
Gt(W)
Ctd(W)
St(W)
Crd(W)

Enter calculation title:
Ex8
```

*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.
8000
843
0

Specify values for:
        P(bar)    T(K)      Y(CO2)
For calculation  2, enter zeros to finish.
8000
853
0

Specify values for:
        P(bar)    T(K)      Y(CO2)
For calculation  3, enter zeros to finish.
8000
863
0

Specify values for:
```

```
     P(bar)   T(K)     Y(CO2)
For calculation 4, enter zeros to finish.
8000
873
0

Specify values for:
     P(bar)   T(K)     Y(CO2)
For calculation 6, enter zeros to finish.
0
0
0
```

(2) Doing the calculation (CONVEX)

Run CONVEX to make the calculation:

```
C:\PERPLEX\Perplex689>convex

Perple_X version 6.8.9, source updated Jan 31, 2020.
Copyright (C) 1986-2020 James A D Connolly <www.perplex.ethz/copyright.html>.

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: hp633ver.dat
Writing print output to file: ex8.plt
Writing plot output to file: ex8.plt
Reading solution models from file: solution_model.dat
Reading Perple_X options from: perplex_option.dat
Writing auto refine summary to: ex8_auto_refine.txt
Writing pseudocompound glossary to: not requested
Writing Perple_X option summary to: not requested
Perple_X computational option settings for CONVEX:
    Keyword:            Value:     Permitted values [default]:
  Auto-refine options:
    auto_refine          aut       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]
    non_linear_switch      F          [F] T
    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  on        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
-------------------------------------------------------------------------------
Summary of make-definition entities:
 fbr      fchum     fphA      fatg      atgts     cumm_dqf     grun_dqf  fanth_dq  ged_dqf   sil8L     fo8L      fa8L      q8L       cfs
cenjh     qjL       fojL      fajL      foTL      faTL      cfsg      mfpv      cmpv      cfpv      capv      fcor      hmgts     foHL      faHL
qHL
-------------------------------------------------------------------------------
-------------------------------------------------------------------------------
Summary of saturated-component entities:
 for: SiO2
  q        trd       crst      coe       stv       qL q8L
  q        trd       crst      coe       stv       qL q8L      qjL       qHL
 for: SiO2  MU
  mu
*solutions may also have compositions consisting entirely of saturated components
-------------------------------------------------------------------------------
**warning ver013** the total amount of the thermodynamic components in: san      is < 0, it will be rejected from the thermodynamic composition space. If non-elemental (e.g., oxide) components are in use this rejection criterion may be incorrect. When this is the case redefine the data base components so that the total amount of the thermodynamic components in san      is > 0.
-------------------------------------------------------------------------------
Solution model summary:
**warning ver114** the following endmembers are missing for Chl(W)
 mnchl    ff3cli    f3clin
**warning ver101** eliminated polytope [Mn][Mn]  during reformulation of Chl(W)      due to mis
```

```
**warning ver102** reformulated polytope [M][M,T]   of Chl(W)     due to missing 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 polytopic 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 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)
  mnbi     ffbi_d   fbi      ftbi_d   tbi
**warning ver101** eliminated polytope [Mn][Mn]  during reformulation of Bi(W)      due to mis
**warning ver102** reformulated polytope [M,T][M]   of Bi(W)      due to missing endmembers.
    286 pseudocompounds generated for: Bi(W)

**warning ver114** the following endmembers are missing for Crd(W)
  mncrd    hmncrd_i
**warning ver050** reformulating polytopic 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:    3214

Summary of included solution models:
Chl(W)   Gt(W)    Ctd(W)   St(W)    Bi(W)    Crd(W)
--------------------------------------------------------------------------------
** Starting exploratory computational stage **
Computing the compositional phase relations at condition  1
cycle          1          1          1
 cycle          2          2          2
…
…
Computing the compositional phase relations at condition  2
 cycle          1          1          1
 cycle          2          2          2
…
…
Computing the compositional phase relations at condition  3
cycle          1          1          1
 cycle          2          2          2
…
…
Computing the compositional phase relations at condition  4
 cycle          1          1          1
```

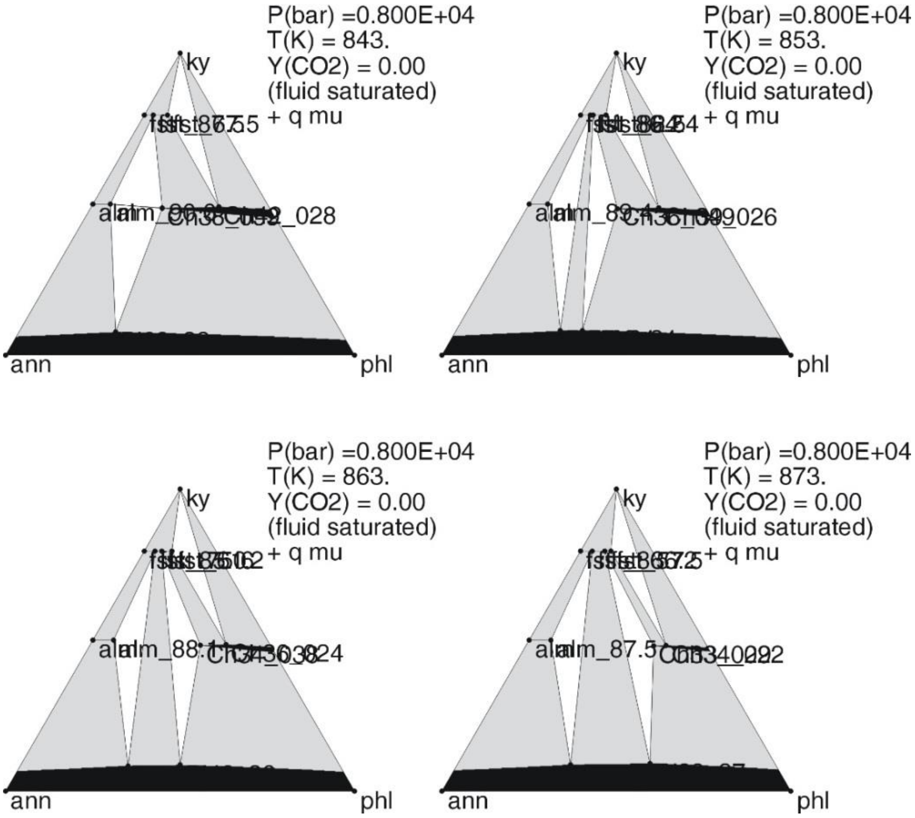
```
 cycle          2          2          2
...
...
Compositions for single-polytope model: Chl(W)
 Simplex 1
    Composition   Minimum        Maximum
    X_Mames      0.11250        0.42500
    X_Mafchl     0.0000         0.0000
    X_Mclin      0.57500        0.88750
 Simplex 2
    Composition   Minimum        Maximum
    X_Mg         0.0000        0.60000
    X_Fe        0.40000         1.0000

Endmember fractions for model: Gt(W)
    Endmember     Minimum        Maximum
    alm          0.87500        0.99375
    py          0.62500E-02     0.12500

Endmember fractions for model: St(W)
    Endmember     Minimum        Maximum
    fst         0.57500        0.99375
    mst          0.62500E-02     0.42500

Compositions for single-polytope model: Bi(W)
 Simplex 1
    Composition   Minimum        Maximum
    X_Mg         0.0000         1.0000
    X_Fe          0.0000         1.0000
 Simplex 2
    Composition   Minimum        Maximum
    X_AlTs       0.0000        0.27500
    X_MBio       0.72500         1.0000
The failure rate during speciation (order-disorder) calculations is   0.000% out of a total of      385820. calculations.
Average number of iterations per speciation calculation:  5.1
```

(3) Plotting the calculated phase diagram (PSVDRAW)

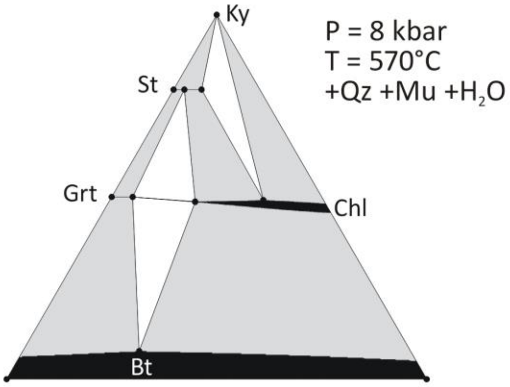
Run PSWDRAW to plot the calculated pseudosection:

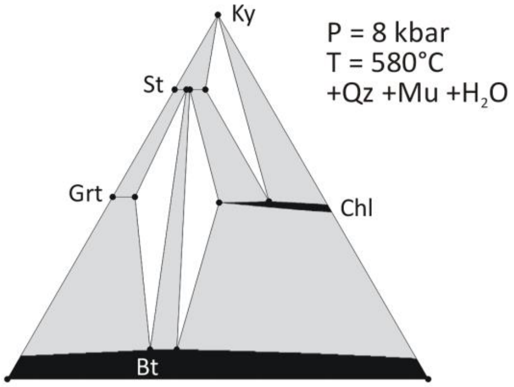
```
C:\PERPLEX\Perplex689>psvdraw

Perple_X version 6.8.9, source updated Jan 31, 2020.
Copyright (C) 1986-2020 James A D Connolly <www.perplex.ethz/copyright.html>.

Enter the project or plot file name [i.e., without the .plt suffix]:
Ex8

Perple_X plot options are currently set as:
   Keyword:             Value:     Permitted values [default]:
   axis_label_scale       1.20       [1.2] (rel)
   bounding_box :
```

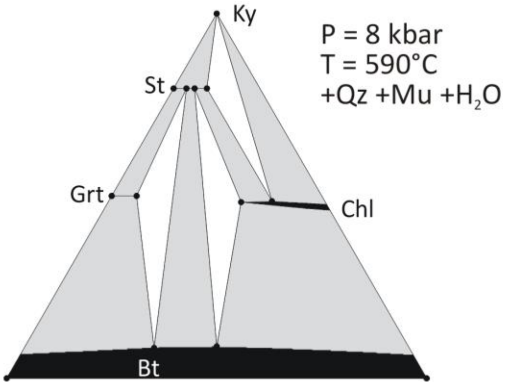
```
                      0     [0] x-min (pts)
                      0     [0] y-min (pts)
                    800     [800] x-length (pts)
                    800     [800] y-length (pts)
   field_fill          T         [T] F
   field_label          T         [T] F
   field_label_scale     0.75       [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
```

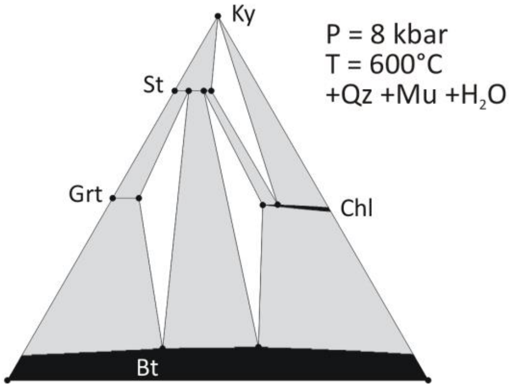


In the resulting diagrams white fields are three-phases fields (+Qz+Mu+H2O), grey fields are two-phases fields (+Qz+Mu+H2O) and black fields are one-phase fields (+Qz+Mu+H2O).









The AFM diagrams predict the stable mineral assemblages and compositions at specific P-T conditions, as a function of the bulk rock composition.

Ex 9

Ex. 9 – 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. 10). At the end, some practical tips for redrawing the PerpleX outputs are given, and the comparison with the AFM chemographies calculated in Ex. 8 will be done.

This exercise also explains how to calculate **compositional ISOPLETHS** and **ISOMODES**.

The 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\Perplex689>build

Perple_X version 6.8.9, source updated Jan 31, 2020.
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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]:
Ex9

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  N2
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  N2
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  N2
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 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

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)?
n

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
…
…
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)
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\Perplex689>vertex

Perple_X version 6.8.9, source updated Jan 31, 2020.
Copyright (C) 1986-2020 James A D Connolly <www.perplex.ethz/copyright.html>.

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

Reading problem definition from file: ex9.dat
Reading thermodynamic data from file: hp633ver.dat
Writing print output to file: ex9.plt
Writing plot output to file: ex9.plt
Writing phase assemblage data to file: ex9.blk
Reading solution models from file: solution_model.dat
Reading Perple_X options from: perplex_option.dat
Writing auto refine summary to: ex9_auto_refine.txt
Writing seismic data options to: ex9_seismic_data.txt
Writing pseudocompound glossary to: ex9_pseudocompound_glossary.txt
Writing Perple_X option summary to: not requested

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
  refinement_switch       F         [T] F
  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]
  non_linear_switch       F         [F] T
  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   on         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      T        [T] F; echo auto-refine compositions
  seismic_data_file     T        [F] T; echo seismic wavespeed options
 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
------------------------------------------------------------------------------
Summary of make-definition entities:
  fbr     fchum    fphA     fatg     atgts    cumm_dqf     grun_dqf  fanth_dq  ged_dqf   sil8L    fo8L     fa8L     q8L      cfs
cenjh     qjL      fojL     fajL     foTL     faTL      cfsg      mfpv      cmpv      cfpv     capv      fcor      hmgts     kjdh      foHL
faHL    qHL     kjL
------------------------------------------------------------------------------
------------------------------------------------------------------------------
Summary of saturated-component entities:
 for: SiO2
  q       trd      crst     coe      stv      qL q8L
  q       trd      crst     coe      stv      qL q8L      qjL      qHL
------------------------------------------------------------------------------
**warning ver099**  no data for aqueous species, aq_output and aq_lagged_speciation disabled.
------------------------------------------------------------------------------
Solution model summary:
**warning ver114** the following endmembers are missing for Chl(W)
 mnchl    ff3cli   f3clin
**warning ver101** eliminated polytope [Mn][Mn]  during reformulation of Chl(W)     due to mis
**warning ver102** reformulated polytope [M][M,T]   of Chl(W)     due to missing 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 polytopic 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 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)
 mnbi     ffbi_d   fbi      ftbi_d   tbi
**warning ver101** eliminated polytope [Mn][Mn]  during reformulation of Bi(W)      due to mis
**warning ver102** reformulated polytope [M,T][M]   of Bi(W)      due to missing endmembers.
   286 pseudocompounds generated for: Bi(W)

**warning ver114** the following endmembers are missing for Crd(W)
 mncrd    hmncrd_i
```

```
**warning ver050** reformulating polytopic 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:    3214

Summary of included solution models:
Chl(W)    Gt(W)     Ctd(W)    St(W)     Bi(W)     Crd(W)
--------------------------------------------------------------------------------
```

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 single-polytope model: Chl(W)
 Simplex 1
   Composition   Minimum       Maximum
   X_Mames     0.16146       0.66146
   X_Mafchl     0.0000        0.0000
   X_Mclin     0.33854       0.83854
 Simplex 2
   Composition   Minimum       Maximum
   X_Mg        0.36458       0.52815
   X_Fe        0.47185       0.63542

Endmember fractions for model: Gt(W)
   Endmember    Minimum       Maximum
   alm        0.73438       0.88021
   py         0.11979       0.26562

Endmember fractions for model: Ctd(W)
   Endmember    Minimum       Maximum
   fctd       0.88021       0.91667
   mctd       0.83333E-01    0.11979

Endmember fractions for model: St(W)
   Endmember    Minimum       Maximum
   fst        0.66667       0.84375
   mst        0.15625       0.33333

Compositions for single-polytope model: Bi(W)
 Simplex 1
   Composition   Minimum       Maximum
   X_Mg        0.42188       0.69792
   X_Fe        0.30208       0.57812
 Simplex 2
   Composition   Minimum       Maximum
   X_AlTs      0.13542       0.43229
   X_MBio      0.56771       0.86458

Compositions for single-polytope model: Crd(W)
 Simplex 1
   Composition   Minimum       Maximum
      1       0.26562       0.46018
      2       0.53982       0.73438
 Simplex 2
   Composition   Minimum       Maximum
      1       0.33333       0.65625
      2       0.34375       0.66667
The failure rate during speciation (order-disorder) calculations is   0.000% out of a total of     4194148. calculations.
Average number of iterations per speciation calculation:  4.2
------------------------------------------------------------------------------
Solution model summary:
   520 pseudocompounds generated for: Chl(W)
     9 pseudocompounds generated for: Gt(W)
     4 pseudocompounds generated for: Ctd(W)
```

```
     10 pseudocompounds generated for: St(W)
    240 pseudocompounds generated for: Bi(W)
    187 pseudocompounds generated for: Crd(W)
Total number of pseudocompounds:     970

Summary of included solution models:
Chl(W)    Gt(W)     Ctd(W)    St(W)     Bi(W)     Crd(W)
--------------------------------------------------------------------------------
```

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.
   584 grid cells to be refined at grid level 2
      ...working (   501 minimizations done)
      ...working (  1003 minimizations done)
      refinement at level 2 involved   1244 minimizations
  4844 minimizations required of the theoretical limit of   14161
  1027 grid cells to be refined at grid level 3
      ...working (   261 minimizations done)
      ...working (   763 minimizations done)
      ...working (  1264 minimizations done)
      ...working (  1765 minimizations done)
      refinement at level 3 involved   1856 minimizations
  6700 minimizations required of the theoretical limit of   56169
  1743 grid cells to be refined at grid level 4
      ...working (   410 minimizations done)
      ...working (   911 minimizations done)
      ...working (  1412 minimizations done)
      ...working (  1914 minimizations done)
      ...working (  2415 minimizations done)
      ...working (  2916 minimizations done)
      refinement at level 4 involved   2916 minimizations
  9616 minimizations required of the theoretical limit of  224676

**warning ver991** The compositions of the following solutions reached internal limits that were automatically relaxed:
    Chl(W)
    Ctd(W)
    St(W)
    Crd(W)
Restriction during the auto-refine stage is usually unimportant. If desired, confirm by comparing the ranges below to those in the *.arf file.
```

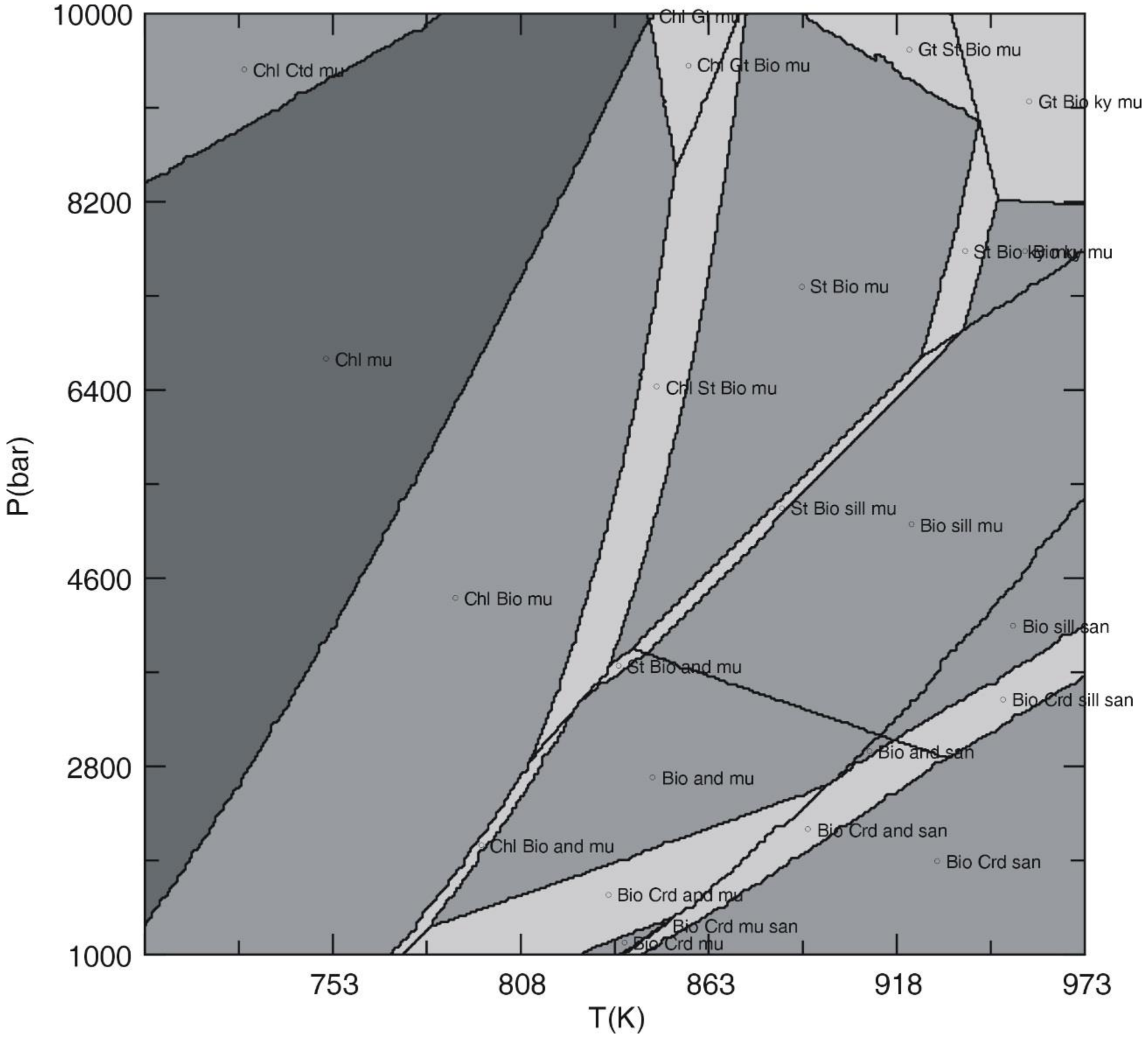
```
NOTE: unintentional restrictions encountered during the exploratory stage may be problematic, refer to the
*_auto_refine.txt file for the exploratory stage warnings.

Compositions for single-polytope model: Chl(W)
 Simplex 1
   Composition  Minimum      Maximum
   X_Mames     0.15712      0.66233
   X_Mafchl    0.86806E-03   0.86806E-03
   X_Mclin     0.33681      0.84201
 Simplex 2
   Composition  Minimum      Maximum
   X_Mg       0.35677      0.52815
   X_Fe       0.47185      0.64323

Endmember fractions for model: Gt(W)
   Endmember   Minimum      Maximum
   alm        0.73351      0.88194
   py         0.11806      0.26649

Endmember fractions for model: Ctd(W)
   Endmember   Minimum      Maximum
   fctd       0.87066      0.91667
   mctd       0.83333E-01   0.12934

Endmember fractions for model: St(W)
   Endmember   Minimum      Maximum
   fst        0.66146      0.85503
   mst        0.14497      0.33854

Compositions for single-polytope model: Bi(W)
 Simplex 1
   Composition  Minimum      Maximum
   X_Mg       0.42101      0.69444
   X_Fe       0.30556      0.57899
 Simplex 2
   Composition  Minimum      Maximum
   X_AlTs     0.13281      0.43056
   X_MBio     0.56944      0.86719

Compositions for single-polytope model: Crd(W)
 Simplex 1
   Composition  Minimum      Maximum
     1       0.25955      0.45976
     2       0.54024      0.74045
 Simplex 2
   Composition  Minimum      Maximum
     1       0.32639      0.65365
     2       0.34635      0.67361
The failure rate during speciation (order-disorder) calculations is   0.000%
out of a total of    13665971. 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\Perplex689>pssect

Perple_X version 6.8.9, source updated Jan 31, 2020.
Copyright (C) 1986-2020 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
--------------------------------------------------------------------------------
Solution model summary:
--------------------------------------------------------------------------------
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
There are   5 fields for: Bio Crd mu san
```



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: light grey = 2-variant fields (6 phases), medium grey = 3-variant fields (5 phases), dark grey = 4-variant fields (4 phases). 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.

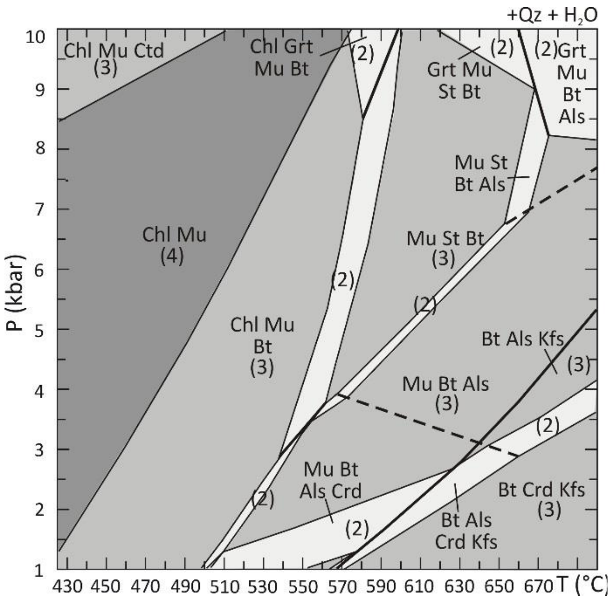
Remember that: F= C – P + 2. In this case: C = 6 (KFMASH)

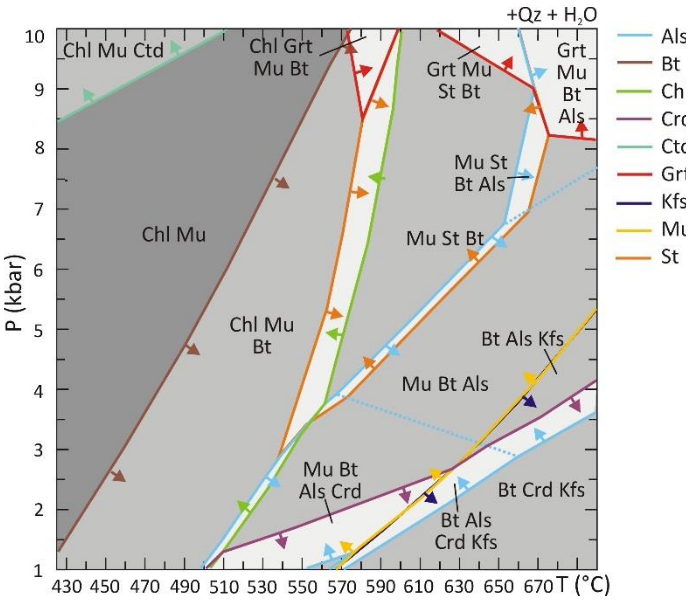
Therefore, fields characterized by 6 phases (P=6; light grey fields in the pseudosection) are di-variant (F=6-6+2); fields with 5 phases (medium grey) are tri-variant and so on.

(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

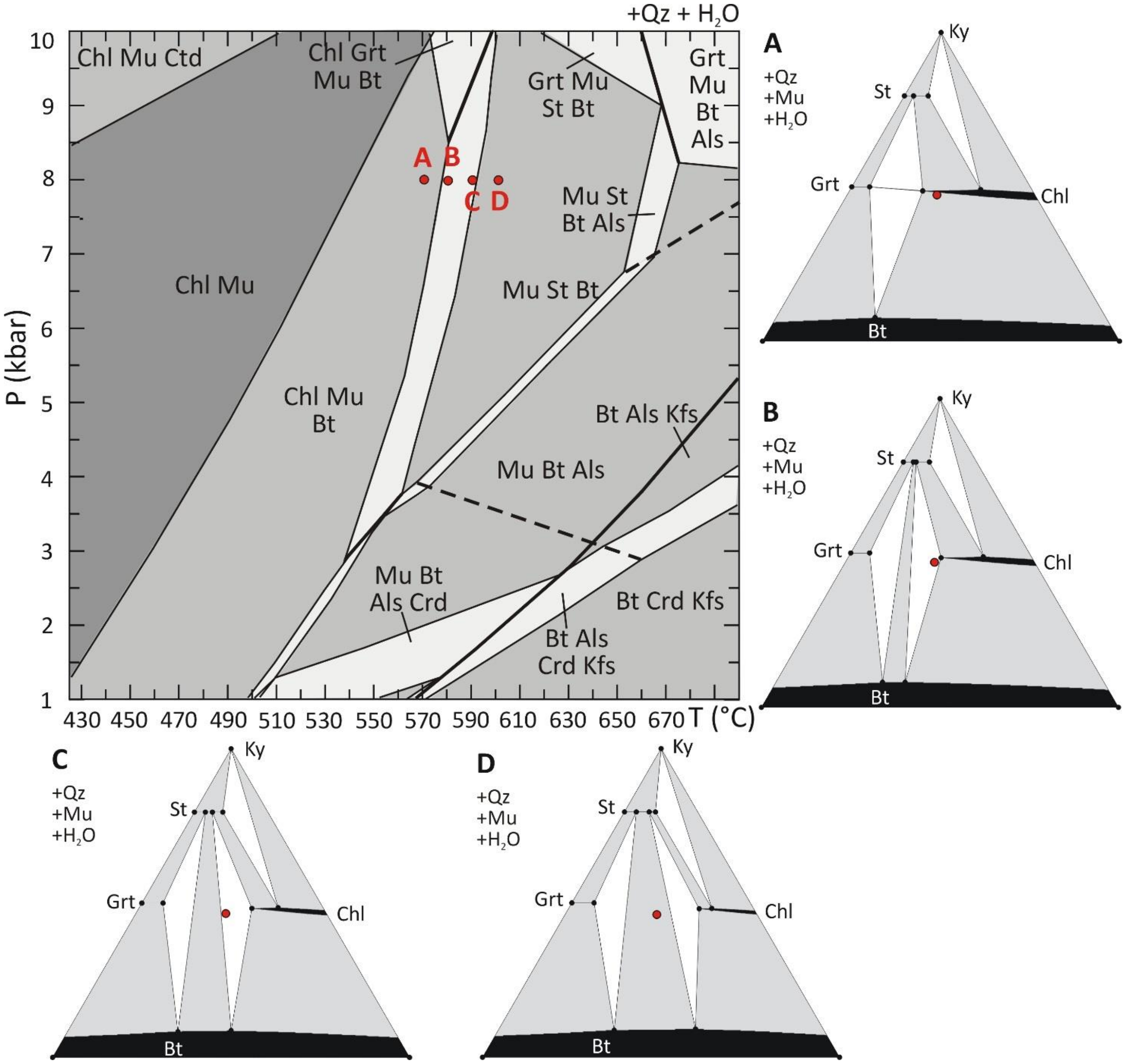




In the diagram on the left, variance of each field is reported in brackets. The thick black lines are true univariant reactions.

In the diagram on the right, the phase-in boundaries are reported with different colours for each phase.

(5) COMPARISON BETWEEN AFM DIAGRAMS AND PSEUDOSECTION



Comparison between AFM diagrams (Ex.8) calculated at P-T conditions A to D and the pseudosection calculated in the KFMASH system (Ex. 9) for a bulk composition K2O=10.18, FeO=24.77 MgO=22.13, Al2O3=42.92 mol% (red dot in the AFM diagrams).

Mineral assemblages predicted by AFM diagrams for this specific bulk rock composition (red dot) must correspond to the assemblages predicted by the P-T pseudosection at the same P-T conditions.

(6) 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\Perplex689>werami

Perple_X version 6.8.9, source updated Jan 31, 2020.
Copyright (C) 1986-2020 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
Writing Perple_X option summary to: not requested

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         mod       [model] abbreviation full
   structural_formulae    T         [T] F
   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         T         [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 wavespeed computational options:
  seismic_data_file      T        [F] T
  bounds                VRH       [VRH] HS
  vrh/hs_weighting       0.5      [0.5] 0->1
  explicit_bulk_modulus  T        [T] F
  poisson_ratio          on       [on] all off; Poisson ratio = 0.35
  seismic_output         som      [some] none all
  poisson_test           F        [F] T
  Tisza_test             F        [F] T
To change these options see: www.perplex.ethz.ch/perplex_options.html
------------------------------------------------------------------------------
Solution model summary:
------------------------------------------------------------------------------

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 “proportions” 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):
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):
mu
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
…
…

Data ranges excluding values equal to bad_number (      NaN) specified in perplex_option.dat:
    Gt(W),vo%       Chl(W),vo%      Ctd(W),vo%      St(W),vo%       Bi(W),vo%       mu,vo%          Crd(W),vo%
ky,vo%        sill,vo%      and,vo%
min       0.793861E-002     0.120039E-001     0.776031E-002     0.999109E-002     0.103286E-001       7.00851
0.236460      0.153644E-001  0.121976E-001  0.267837E-002
max     14.4877        42.3855        2.20469        27.3600        66.0825        57.7831        59.7448        25.8172
29.4427        29.8888
Output has been written to the 2d tab format file: ex9_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
```

At the end, you have a new file (ex9_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 chlorite, staurolite, garnet and biotite is calculated.

```
C:\PERPLEX\Perplex689>werami

Perple_X version 6.8.9, source updated Jan 31, 2020.
Copyright (C) 1986-2020 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
Writing Perple_X option summary to file: not requested

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         mod       [model] abbreviation full
   structural_formulae    T         [T] F
```

```
   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        T        [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 wavespeed computational options:
   seismic_data_file     T        [F] T
   bounds                VRH      [VRH] HS
   vrh/hs_weighting      0.5      [0.5] 0->1
   explicit_bulk_modulus  T       [T] F
   poisson_ratio         on       [on] all off; Poisson ratio = 0.35
   seismic_output        som      [some] none all
   poisson_test          F        [F] T
   Tisza_test            F        [F] T
 To change these options see: www.perplex.ethz.ch/perplex_options.html
 ------------------------------------------------------------------------------
 Solution model summary:
 ------------------------------------------------------------------------------
 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.
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         | index for MgO
1         | weighting factor for MgO
4         | index for FeO
1         | weighting factor for FeO

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):
Chl(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[Chl(W)2]     C[St(W)3]     C[Bi(W)4]
min   0.118056       0.471855       0.144965       0.305556
max   0.266493       0.643229       0.338542       0.578993
Output has been written to the 2d tab format file: ex9_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 (ex9_2.tab) in the Perple_X folder.

(7) Plotting isomodes and compositional isopleths (PYWERAMI)

Use PYWERAMI to plot the calculated isomodes and compositional isopleths.

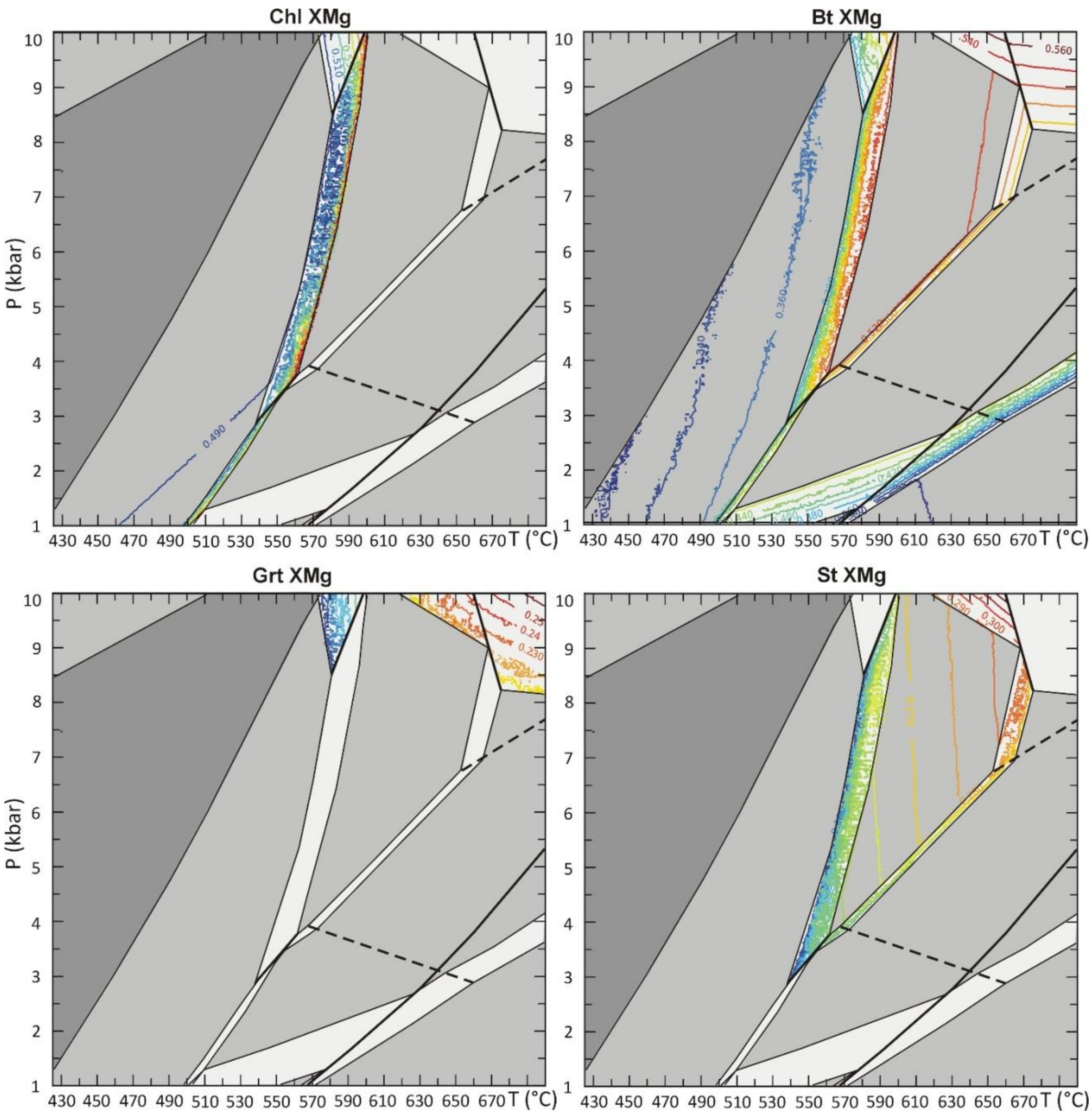
You can download Pywerami at this link from the Perple_X website (PyWerami - a free alternative to MatLab): https://petrol.natur.cuni.cz/~ondro/oldweb/pywerami:home
Install Pywerami on your pc.

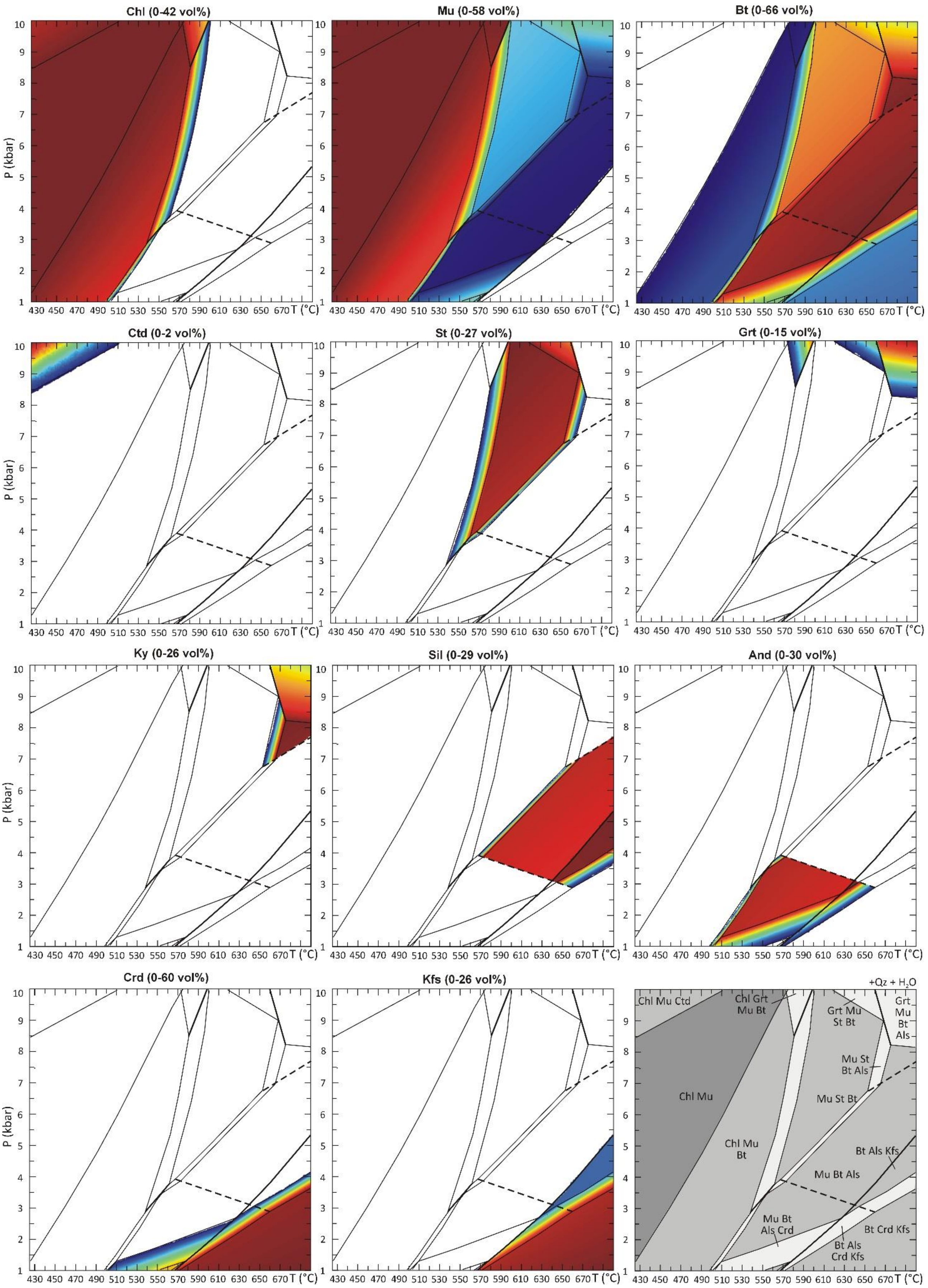
Run PYWERAMI to plot isopleths and isomodes.

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(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.




Chl (0-42 vol%)
Mu (0-58 vol%)
Bt (0-66 vol%)
Ctd (0-2 vol%)
St (0-27 vol%)
Grt (0-15 vol%)
Ky (0-26 vol%)
Sil (0-29 vol%)
And (0-30 vol%)
Crd (0-60 vol%)
Kfs (0-26 vol%)
P (kbar)
T (°C)
430 450 470 490 510 530 550 570 590 610 630 650 670
1 2 3 4 5 6 7 8 9 10
+Qz + H₂O
Chl Mu Ctd
Chl Grt Mu Bt
Grt Mu St Bt
Grt Mu Bt Als
Mu St Bt Als
Chl Mu
Mu St Bt
Chl Mu Bt
Bt Als Kfs
Mu Bt Als
Mu Bt Als Crd
Bt Crd Kfs
Bt Als Crd Kfs

Ex 10

Ex.10 – P-T pseudosection for a METAPELITE in the MnNKCFMASH system

This exercise is intended to explore the influence of some minor components (Na_2O, CaO and MnO) on the topology of the pseudosection calculated for the metapelite sample investigated in Ex. 9. The exercise also explains how to calculate **CUMULATIVE MODES along a geothermal gradient**.

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. 9, except for the addition of Na2O, CaO and MnO components **you can edit the ex9.dat input file** (remember to re-name the file as Ex10). 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) and the white mica (muscovite + paragonite) solid solution models should be added to the calculation.

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

(2) Doing the calculation (VERTEX)

Run VERTEX to make the calculation:

```
C:\PERPLEX\Perplex689>vertex

Perple_X version 6.8.9, source updated Jan 31, 2020.
```

```
Copyright (C) 1986-2020 James A D Connolly <www.perplex.ethz/copyright.html>.

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\Perplex689>pssect

Perple_X version 6.8.9, source updated Jan 31, 2020.
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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
--------------------------------------------------------------------------------
Solution model summary:
--------------------------------------------------------------------------------
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
There are   5 fields for: Fsp Fsp Mica Bio Crd
There are   9 fields for: Fsp Gt Mica St Bio sill
There are   5 fields for: Fsp Gt Mica St Bio ky
There are  14 fields for: Fsp Chl Mica Bio zo ab
There are   4 fields for: Fsp Chl Gt Mica Bio zo ab
```

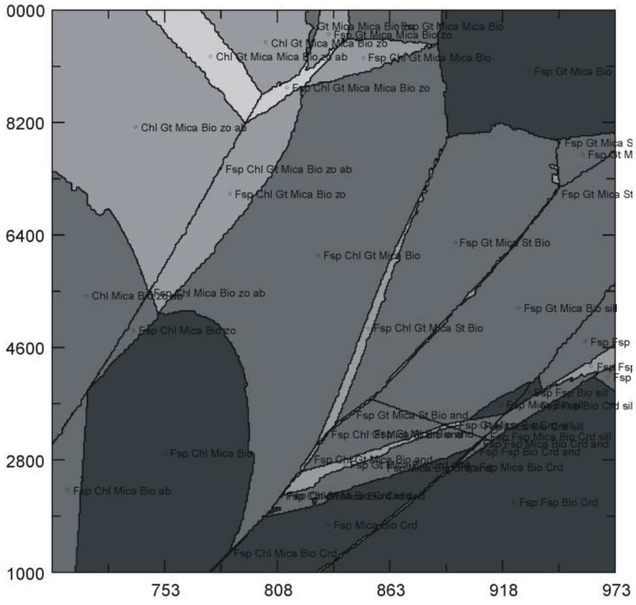
In the resulting diagram, both plagioclase and K-feldspar are reported as "feldspar". Thus, fields containing two feldspars contain both plagioclase and K-feldspar, whereas those containing one feldspar can contain either plagioclase or K-feldspar. **To know which of the two feldspars is stable in a given field, use WERAMI option 1 (properties at specified conditions)**, e.g. at 753 K, 3000 bar:

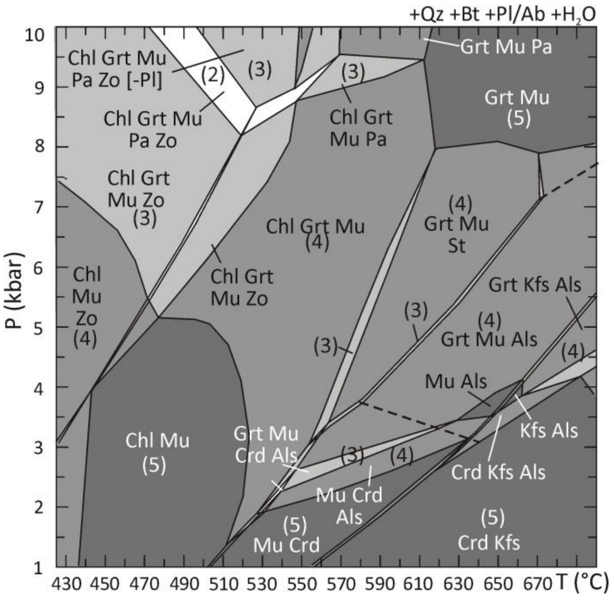
```
Stable phases at:
                 T(K)     =  753.000
                 P(bar)   =  3000.00
                 Y(CO2)   =  0.00000

Phase Compositions (molar  proportions):
          wt %    vol %   mol %    mol      Na2O     MgO      Al2O3    K2O      CaO      MnO      FeO      SiO2     H2O
Fsp       27.70   29.75   39.80   15.7    0.34089  0.00000  0.65651  0.00260  0.31301  0.00000  0.00000  2.68699  0.00000
Chl       17.66   17.11   10.85   4.28    0.00000  2.58176  1.22842  0.00000  0.00000  0.05789  2.13193  2.77158  4.00000
Mica      31.79   32.05   30.76   12.1    0.06219  0.03171  1.44604  0.43645  0.00272  0.00000  0.02360  3.05260  1.00000
Bio       22.85   21.09   18.59   7.34    0.00000  1.10997  0.66190  0.50000  0.00000  0.02344  1.70469  2.83810  1.00000

Phase speciation (molar proportions):
Fsp          abh: 0.68178, an: 0.31301, san: 0.00521
Chl          mnchl: 0.01158, daph: 0.46485, ames: 0.22927, afchl: 0.19442, clin: 0.29344, och1: 0.00031, och2: -0.19388
Mica         mu: 0.81759, pa: 0.12437, ma1_dqf: 0.00272, cel: 0.03171, fcel: 0.02360
Bio          mnbi: 0.00781, east: 0.16190, ann: 0.57357, phl: 0.27273, obi: -0.01602
Structural formulae for 688 format solution models:
```

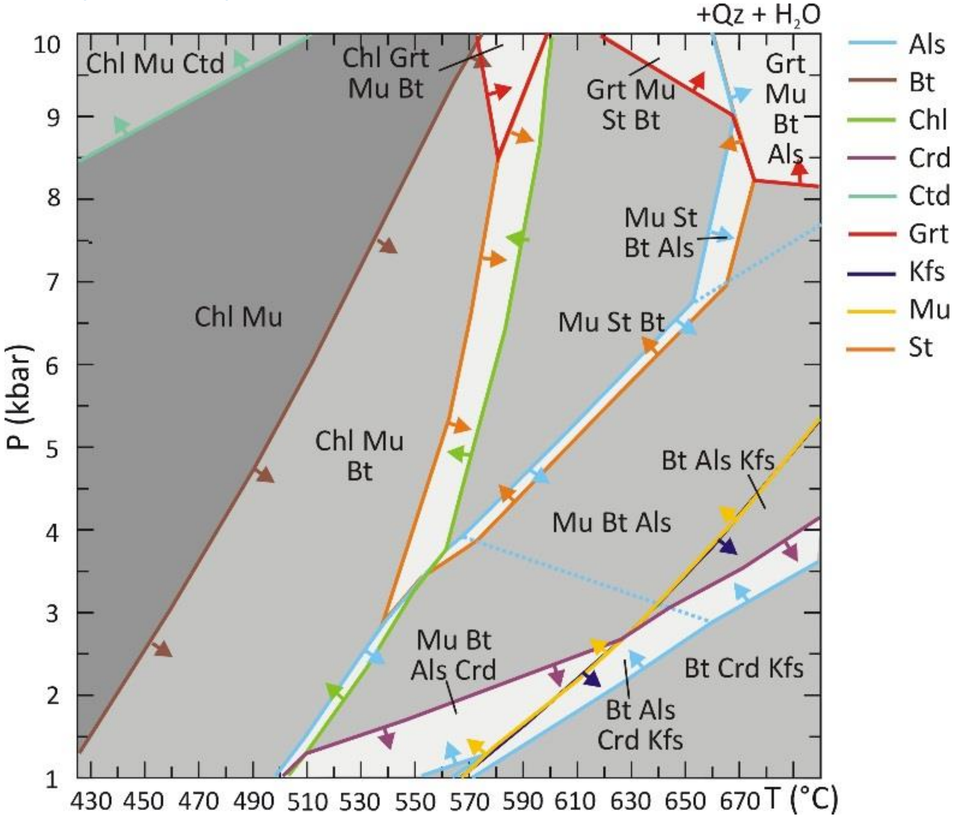
The feldspar stable at 753 K, 3000 bar is a plagioclase.



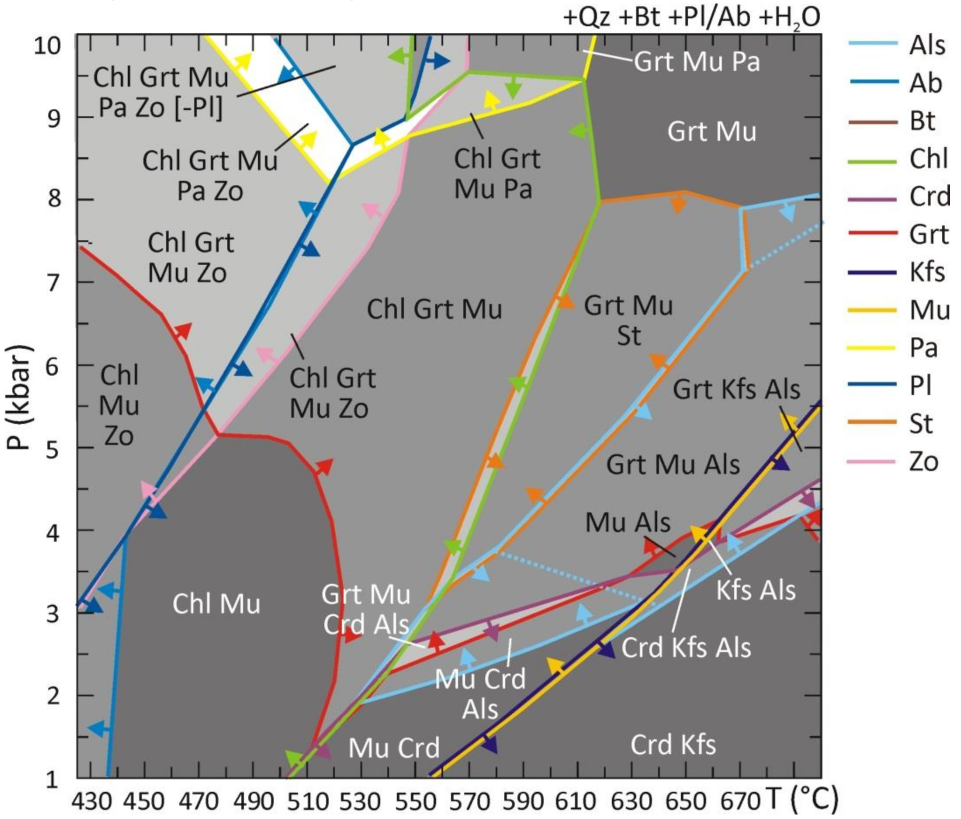


In the diagram on the right, variance of each field is reported in brackets.

Ex.9 (KFMASH)



Ex. 10 (MnNCKFMASH)

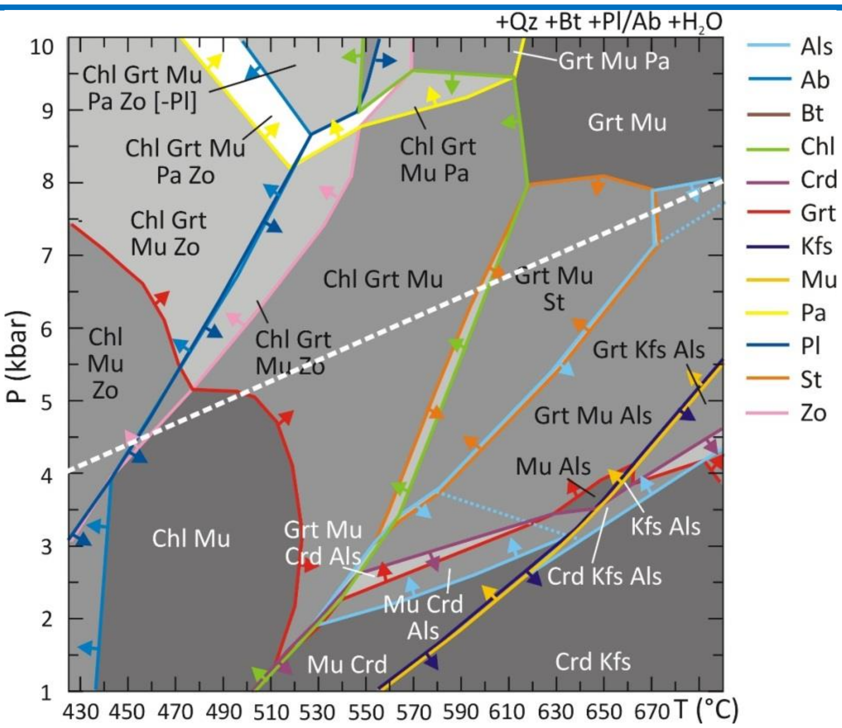


Comparing this pseudosection with that modelled in Ex. 9 (KFMASH system), it appears that the introduction of Na_2O, CaO and MnO has the following consequences:

- **The garnet stability field is significantly enlarged toward low P and T with respect to the pseudosection of Ex. 9;**
- **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 and/or albite is predicted to be stable in most of the fields;**
- **Zoisite appears at low T.**

(4) Calculating cumulative modes along a geothermal gradient (WERAMI)

This section explains how to calculate the **variation in the modal amounts** of all the phase (vol%) along a geothermal gradient defined as: P (bar) = 15 T (K) – 6545 (corresponding to the white dashed line reported in the pseudosection below).



Use an excel spreadsheet to create the input file for the definition of the P/T gradient. The input file should consist of two columns only, i.e. the first column contains the temperatures (in Kelvin), the second column contains the pressures (in bar). Consider the temperatures range 430-700°C (703-973 K), and temperature values with an interval of 1°C; derive pressure values according to the equation P (bar) = 15 T (K) – 6545. Save the file as a .txt file named “grad.txt”,

Run WERAMI to calculate the MODES of ALL the phases.

```
C:\PERPLEX\Perplex689>werami

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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
Writing Perple_X option summary to: not requested
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            T         [F] T
  fancy_cumulative_modes F         [F] T
  interpolation         on        [on] off
  melt_is_fluid         F         [F] T
  solution_names        abb       [model] abbreviation full
  structural_formulae    T         [T] F
  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        T         [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 wavespeed computational options:
  seismic_data_file     T         [F] T
  bounds                VRH       [VRH] HS
  vrh/hs_weighting      0.5       [0.5] 0->1
  explicit_bulk_modulus  T         [T] F
  poisson_ratio         on        [on] all off; Poisson ratio = 0.35
  seismic_output        som       [some] none all
  poisson_test          F         [F] T
  Tisza_test            F         [F] T
To change these options see: www.perplex.ethz.ch/perplex_options.html
------------------------------------------------------------------------------
Solution model summary:
------------------------------------------------------------------------------
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
4
```

Select option 4 if you would like to use the geothermal gradient as defined in the grad.txt file.

```
Path will be described by:
  1 - a file containing a polynomial function
  2 - a file containing a list of x-y points
Enter 1 or 2:
2

Enter the file name:
grad.txt

File contains   271 points
every nth plot will be plotted, enter n:
1
```

Here you can specify if you want to use all the P-T points defined in the input file, or if you want to use a different P(T) interval. Answering 1 means that you want to use all the points as defined in the input file.

```
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
25
```

Option 25 allows to simultaneously calculate the mode of all the phases.

```
Output cumulative modes (y/n)?
(see www.perplex.ethz.ch/perplex_options.html#cumulative_modes)
n
```

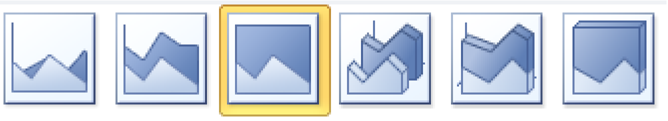
Although our aim is to calculate CUMULATIVE MODES, I suggest to not select the “cumulative mode” option here, because it is more easy to plot “normal” modes (i.e. not cumulative) using EXCEL rather than the “cumulative” modes using PSSECT.

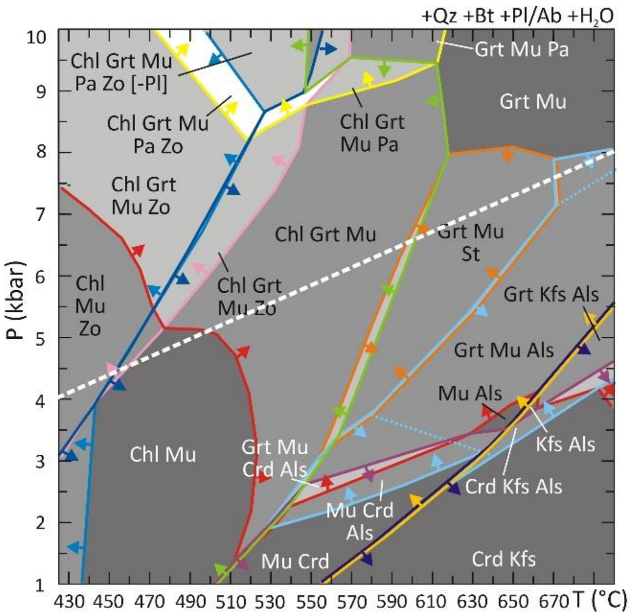
```
Include fluid in computation of aggregate (or modal) properties (y/n)?
n

**warning ver178** at T(K)=   703.0     P(bar)=   4000.
the shear modulus of: Chl
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:
     Fsp          Fsp          Chl          Mica          Mica          Bio          ab          zo          Gt
min     27.9798       0.100000E+100  0.131809        20.7551       0.100000E+100  13.2322        20.2230       0.103964
0.568945E-1
max     31.3606      -0.100000E+100   21.5735        38.3471      -0.100000E+100   37.3788        20.5769        6.29250
14.7562

Output has been written to two files:
   plt format is in file: ex10_1.plt
   1d tab format is in file: ex10_1.tab
plt format files can be plotted with:
   PSVDRAW
1d tab format files can be processed with:
   PSTABLE - a Perple_X plotting program
   PERPLE_X_PLOT - a Matlab plotting script
   spread-sheet programs, e.g., EXCEL
```

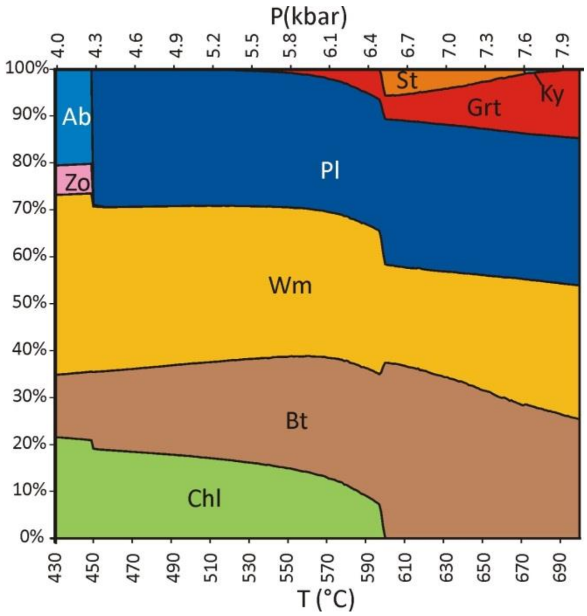
```
for details on tab format refer to:
  perplex.ethz.ch/perplex/faq/Perple_X_tab_file_format.txt

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 (ex10_1.tab) in the Perple_X folder.

You can open the ex10_1.tab file using EXCEL; replace the NaN values with 0 and plot the data using the option Area Graph.







Ex 11

Ex. 11 – 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. 9 and 10.

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. 10 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=0.00, 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. 10

In the perplex_option file, change the solution_names keyword in “abb”, in order to show – in the output - the abbreviation name (rather than the whole model name) for solution models .

(1) Definition of the problem (BUILD)

```
C:\PERPLEX\Perplex689>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]:
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 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 N2 ZnO
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  N2 ZnO
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 ZnO
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.

NOTE: the EoS choice specified here will override the EoS choice specified by the hybrid_EoS option, tooverride this behavior delete the special_component section from the 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         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

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)?
N

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
biotite models:          Bio(TCC)   Bi(W)      Bi(HGP)    Bio(WPH)   Bio(HP)
ternary-feldspar models:  feldspar   feldspar_B Pl(I1,HP)  Fsp(C1)
…
…
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:
Ex11
```

(2) Doing the calculation (VERTEX)

Run VERTEX to make the calculation:

```
C:\PERPLEX\Perplex689>vertex

Perple_X version 6.8.9, source updated Jan 31, 2020.
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Enter the project name (the name assigned in BUILD) [default = my_project]:
Ex11
….
```

(3) Plotting the calculated phase diagram (PSSECT)

Run PSSECT to plot the calculated pseudosection:

```
C:\PERPLEX\Perplex689>pssect

Perple_X version 6.8.6, source updated Jan 31, 2020.
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Enter the project name (the name assigned in BUILD) [default = my_project]:
Ex11

Reading Perple_X options from: perplex_option.dat
-----------------------------------------------------------------------------
Solution model summary:
-----------------------------------------------------------------------------
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)
```
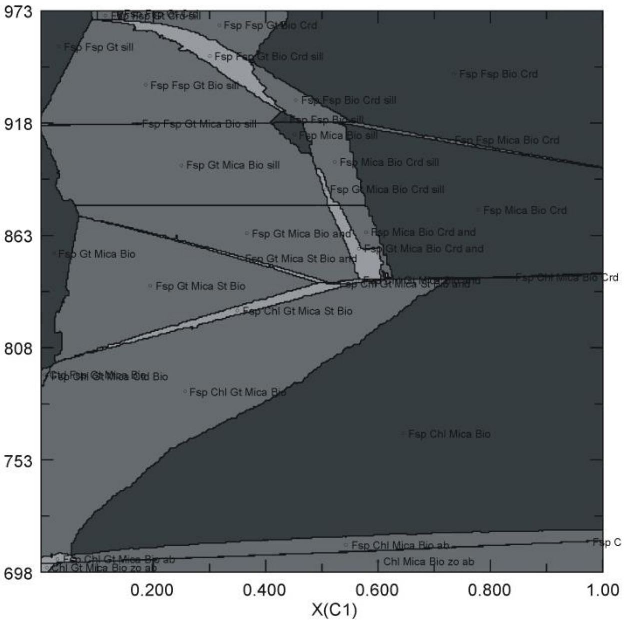
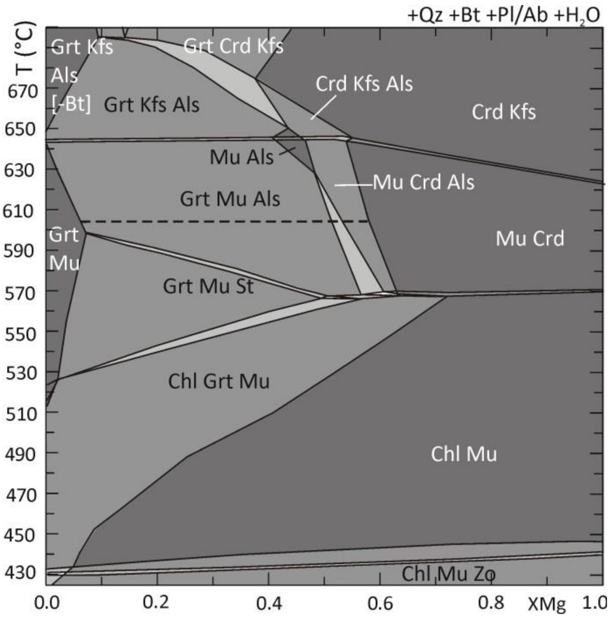
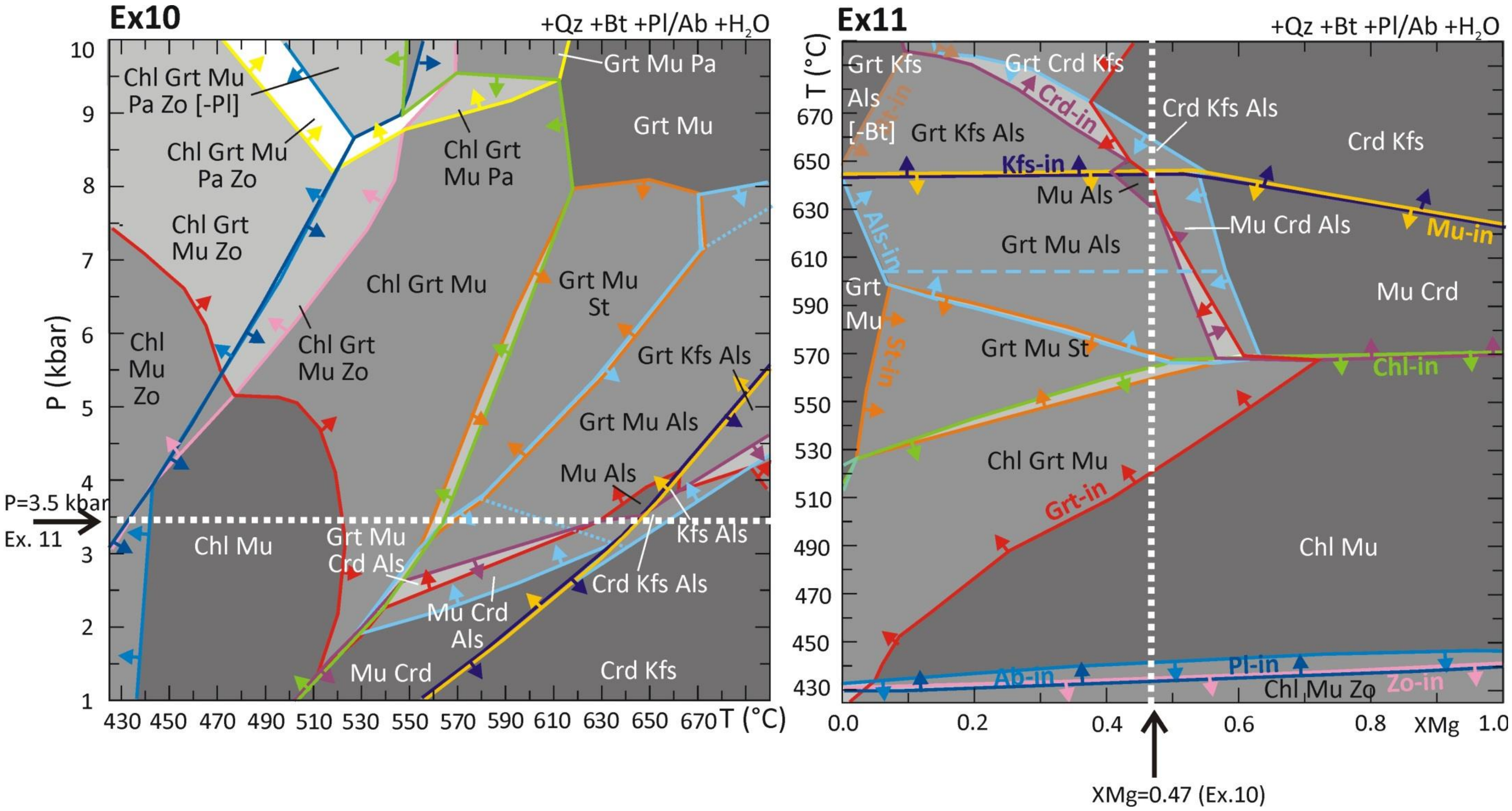

```
    plot_aspect_ratio      1.000      [1.0] x_axis_length/y_axis_length
    replicate_label        0.250      0->1 [0.025]
    splines                T          [T] F
    tenth_ticks            F          [F] T
    text_scale             1.000      [1.] (rel)
 To change these options edit or create 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
 There are   2 fields for: Fsp Fsp Gt Mica Bio sill
 There are  17 fields for: Fsp Chl Mica Bio zo ab
 There are   2 fields for: Fsp Chl Gt Mica Ctd Bio
```







Comparison between the P-T pseudosection calculated in Ex. 10 (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 12

Ex. 12 – 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, including its initial H_2O amount (which is generally not the case…). 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\Perplex689>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]:
ex12

The problem definition file will be named: ex12.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  N2 ZnO
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 N2
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 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

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 ver056** the EoS specified for H2O by the hybrid_EoS option will overridden by the EoS specified in the
problem definition file. To prevent this behavior delete the special_component section from the header of the
thermodynamic data file.

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

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
biotite models:          Bio(TCC)  Bi(W)     Bi(HGP)    Bio(WPH)   Bio(HP)
ternary-feldspar models:  feldspar   feldspar_B Pl(I1,HP)  Fsp(C1)
…
…
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:
Ex12
```

(2) Doing the calculation (VERTEX)

Run VERTEX to make the calculation:

```
C:\PERPLEX\Perplex689>vertex

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Enter the project name (the name assigned in BUILD) [default = my_project]:
Ex12

…
…
**error ver180** too many pseudocompounds  2888888 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 perplex_option.dat
  - restrict the subdivision range for the solution
  - if nonlinear subdivision is specified for the solution then increase the resolution parameters or change to
linear subdivision
  - increase parameter k13 and recompile

NOTE!! melt(W)    specifies nonlinear subdivision schemes, the number of pseudo-compounds generated by
nonlinear subdivision is independent of initial_resolution unless the non_linear_switch option is T (true).
For additional information on nonlinear subdivision refer to the commentary in the header of the solution
model file. If you do not understand nonlinear subdivision use linear subdivision.

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: **1/9 (exploratory stage) and 1/14 (auto-refine stage)**.

```
initial_resolution 1/9 1/14 |[1/16 1/48]*>0,<1 resolution for static compositions
```

I suggest to rename the perplex_option file (e.g. perplex_option_ex12.dat); **remember to change the name of the perplex_option file in the input file**.

Run again VERTEX

```
C:\PERPLEX\Perplex689>vertex

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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\Perplex689>pssect

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Enter the project name (the name assigned in BUILD) [default = my_project]:
Ex12

Reading Perple_X options from: perplex_option.dat
------------------------------------------------------------------------------
Solution model summary:
------------------------------------------------------------------------------
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
```
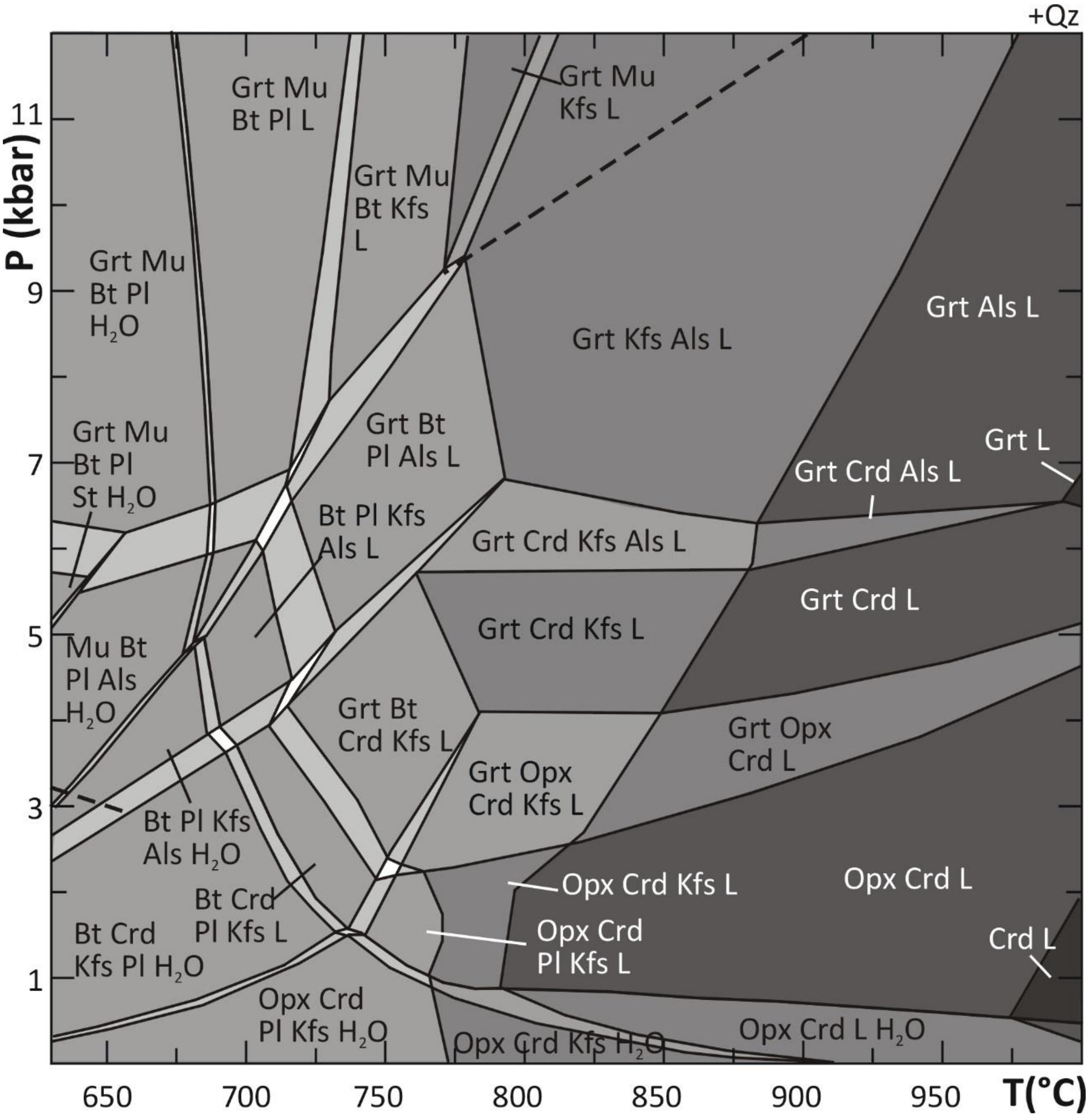
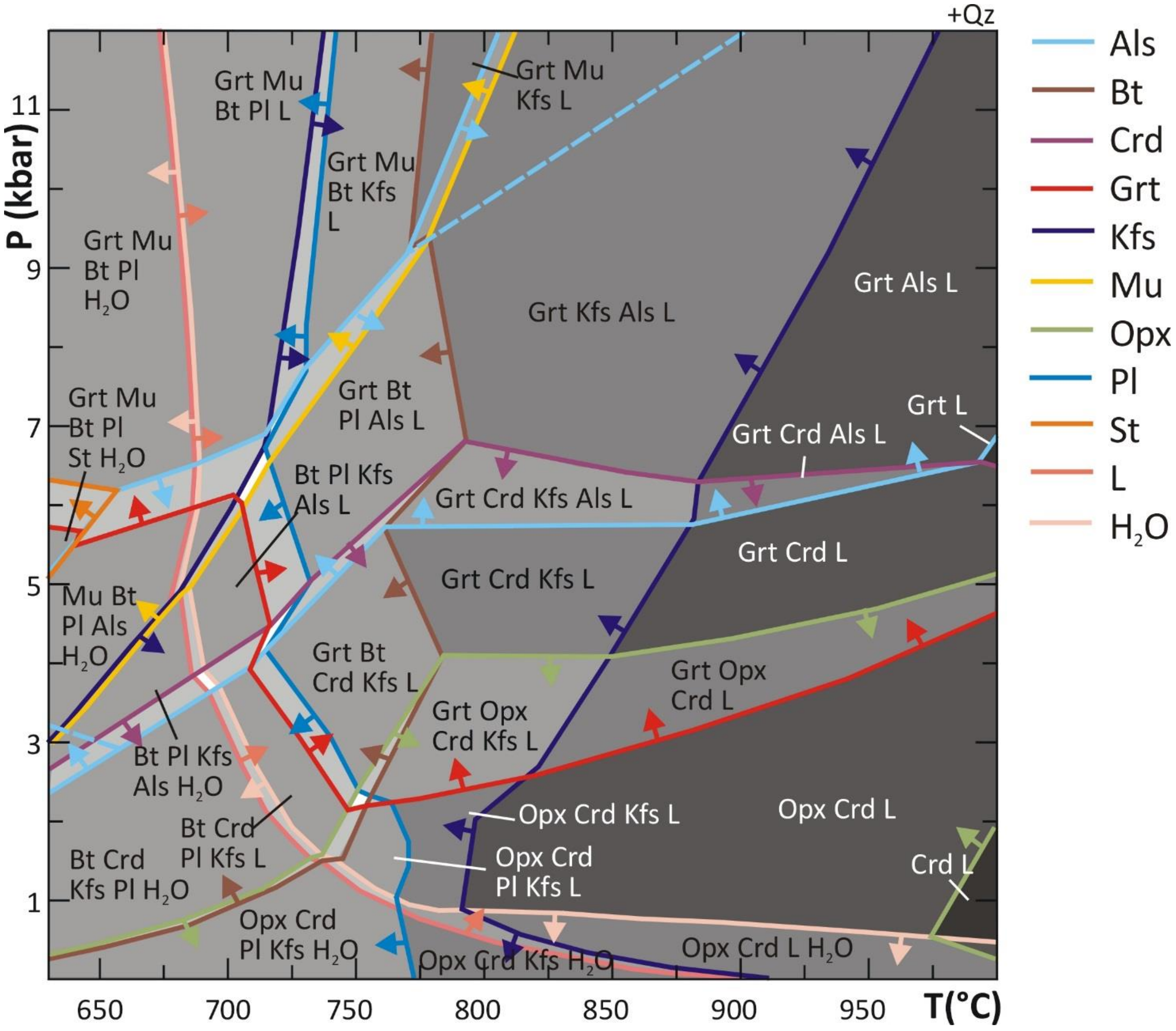

```
    line_width           1.00      0-99 [1.] (pts)
    picture_transformation :
                          0.180    [0.18] x-scale (rel)
                          0.180    [0.18] y-scale (rel)
                           130.    [0.18] x-translation (pts)
                           220.    [0.18] y-translation (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: ex12.ps

Modify the default plot (y/n)?
n

There are   9 fields for: Fsp Fsp Mica Bio sill H2O
There are  10 fields for: Fsp Fsp Opx Bio Crd H2O
There are   3 fields for: Fsp Fsp Gt Melt Opx Crd
```


+Qz
P (kbar)
11
9
7
5
3
1
650
700
750
800
850
900
950
T(°C)
Grt Mu Bt Pl L
Grt Mu Kfs L
Grt Mu Bt Kfs L
Grt Mu Bt Pl H_2O
Grt Kfs Als L
Grt Als L
Grt Bt Pl Als L
Grt Mu Bt Pl St H_2O
Bt Pl Kfs Als L
Grt L
Grt Crd Als L
Grt Crd Kfs Als L
Grt Crd L
Grt Crd Kfs L
Mu Bt Pl Als H_2O
Grt Bt Crd Kfs L
Grt Opx Crd L
Grt Opx Crd Kfs L
Bt Pl Kfs Als H_2O
Opx Crd Kfs L
Opx Crd L
Bt Crd Pl Kfs L
Opx Crd Pl Kfs L
Bt Crd Kfs Pl H_2O
Crd L
Opx Crd Pl Kfs H_2O
Opx Crd Kfs H_2O
Opx Crd L H_2O



(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\Perplex689>werami

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

ex12

```
Reading Perple_X options from: perplex_option_ex12.dat
Writing Perple_X option summary to: not requested

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
    structural_formulae    T          [T] F
    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          T         [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 wavespeed computational options:
    seismic_data_file       T         [F] T
    bounds                  VRH       [VRH] HS
    vrh/hs_weighting        0.5       [0.5] 0->1
    explicit_bulk_modulus  T          [T] F
    poisson_ratio           on        [on] all off; Poisson ratio = 0.35
```

```
   seismic_output        som        [some] none all
   poisson_test           F         [F] T
   Tisza_test             F         [F] T
To change these options see: www.perplex.ethz.ch/perplex_options.html

**warning ver056** the EoS specified for H2O      by the hybrid_EoS option will be overridden by the EoS specified in
the problem definition file. To prevent this behavior delete the special_component section from the header of the
thermodynamic data file.
-----------------------------------------------------------------------------
Solution model summary:
-----------------------------------------------------------------------------
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 and/or melt 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   0.790   0.009   0.579   0.000   0.202   2.421

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 based on the maximum anorthite content (and, conversely, if you want to calculate the isomodes for K-feldspar, it should be identified based 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
```

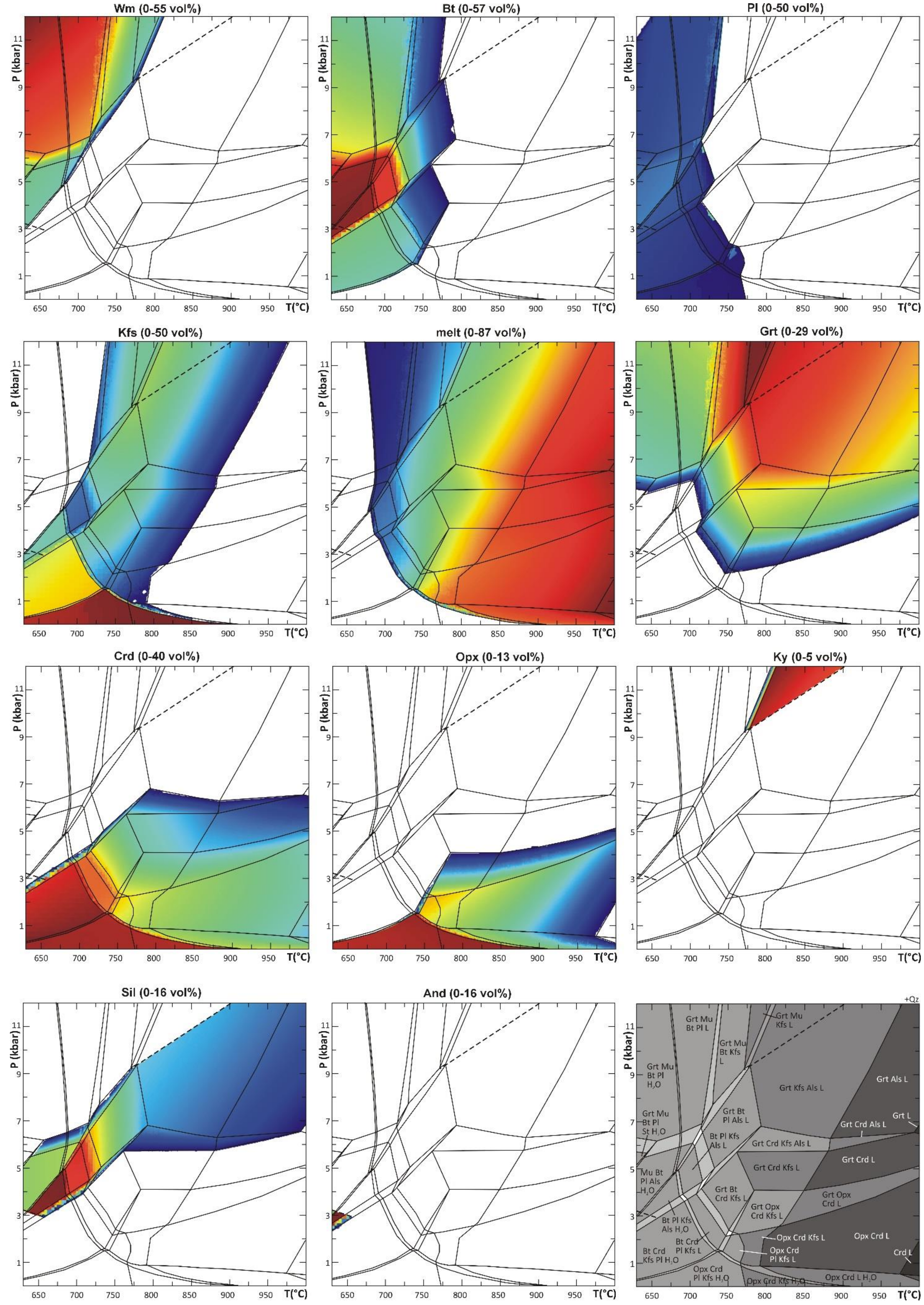
Remember that you are calculating the isomodes of plagioclase in those fields where two feldspar coexist. In the fields where you have only one feldspar, the calculated isomodes refer to either Pl or Kfs, depending on which one is stable.

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.

```
**warning ver637** Immiscibility occurs in one or more phases. Interpolation will be turned off at all affected nodes.
override this feature at the risk of computing inconsistent properties by setting the option warning_ver637 to F and
restarting WERAMI.

Data ranges excluding values equal to bad_number (       NaN) specified in perplex_option.dat:
    melt(W),vo%     Mica(W),vo%     Bi(W),vo%      feldspar,vo%   Gt(W),vo%      Crd(W),vo%      Opx(W),vo%      ky,vo%
sill,vo%      and,vo%
min   0.141585E-001  0.150724E-002  0.190068E-002  0.328269E-003  0.143568E-003  0.179418E-002  0.649021E-004
0.784024E-002  0.596887E-003  0.446749E-001
max    86.7795       54.9220       56.8175       49.9211       29.3695       39.5435       12.8703       5.06310       15.8456
16.1452
Output has been written to the 2d tab format file: ex12_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
```

At the end, you have a new file (ex12_1.tab) in the Perple_X folder.

Run again WERAMI to calculate isomodes for K-feldspar (ex12_2.tab).


Wm (0-55 vol%)
Bt (0-57 vol%)
Pl (0-50 vol%)
Kfs (0-50 vol%)
melt (0-87 vol%)
Grt (0-29 vol%)
Crd (0-40 vol%)
Opx (0-13 vol%)
Ky (0-5 vol%)
Sil (0-16 vol%)
And (0-16 vol%)
P (kbar)
1
3
5
7
9
11
650
700
750
800
850
900
950
T(°C)
+Qz
Grt Mu Bt Pl L
Grt Mu Kfs L
Grt Mu Bt Kfs L
Grt Mu Bt Pl H_2O
Grt Kfs Als L
Grt Als L
Grt Mu Bt Pl St H_2O
Grt Bt Pl Als L
Bt Pl Kfs Als L
Grt L
Grt Crd Als L
Grt Crd Kfs Als L
Grt Crd L
Grt Crd Kfs L
Mu Bt Pl Als H_2O
Grt Bt Crd Kfs L
Grt Opx Crd L
Grt Opx Crd Kfs L
Bt Pl Kfs Als H_2O
Opx Crd Kfs L
Opx Crd L
Bt Crd Pl Kfs L
Opx Crd Pl Kfs L
Bt Crd Kfs Pl H_2O
Crd L
Opx Crd Pl Kfs H_2O
Opx Crd Kfs H_2O
Opx Crd L H_2O

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
Fsp         6.63     7.66     9.59    3.00    0.00000  0.00000  0.58422  0.02451  0.16843  0.00000  0.39128  2.83157
Gt         18.86    13.85    15.14    4.73    0.00000  0.54448  1.00000  0.00000  0.08672  2.36880  0.00000  3.00000
Melt        2.73     3.89    10.24    3.20    0.65118  0.00118  0.13515  0.04163  0.00410  0.00376  0.08089  1.12677
Mica       40.89    43.86    39.48    12.3    1.00000  0.05194  1.40112  0.45699  0.00343  0.04865  0.04129  3.09716
Bio        30.89    30.75    25.55    7.98    1.00000  1.19326  0.81172  0.50000  0.00000  1.49502  0.00000  2.68828

Phase speciation (molar proportions):
Fsp         abh: 0.78255, an: 0.16843, san: 0.04902
Gt          alm: 0.78960, py: 0.18149, gr: 0.02891
Melt        fo8L: 0.00030, fa8L: 0.00094, abL: 0.16178, sil8L: 0.00533, anL: 0.00410, kspL: 0.08327, q8L: 0.09311
          h2oL: 0.65118
Mica        mu: 0.81339, pa: 0.08259, ma1_dqf: 0.00343, cel: 0.05194, fcel: 0.04865
Bio         east: 0.31172, ann: 0.53443, phl: 0.26212, obi: -0.10827
```

Ex 13

Ex. 13 – INDIRECT modelling of an anatectic METAPELITE

In Ex. 12 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?

- The observed mineral assemblage
- The measured mineral compositions
- The measured bulk composition (which often does not coincide with the composition of the protolith!)

What we do not know?

- The bulk composition of the protolith (if a certain amount of melt was lost during the prograde evolution)
- 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**.

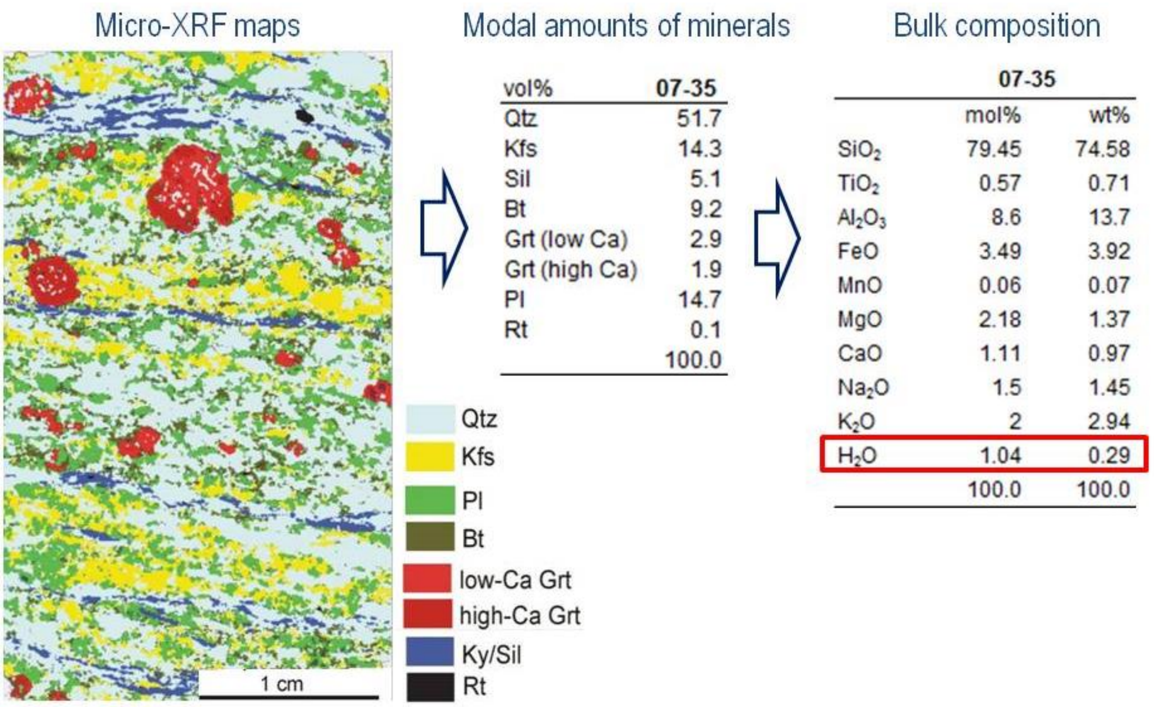
Ex. 13.1 – P-T EVOLUTION from PEAK conditions to FINAL MELT CRYSTALLIZATION

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.



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

	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%):

SiO_2=79.45; TiO_2: 0.57; Al_2O_3=8.6, FeO=3.49, MgO=2.18, CaO=1.11, Na_2O=1.5, K_2O=2.00, H_2O=1.04

T=700-900°C

P=3-15 kbar

Because the problem is similar to that of Ex. 12, we can try to skip the BUILD session and to directly edit the input file, starting from that of Ex. 12 (Use the perplex_option_ex12.dat file created for Ex12).

NB: SiO_2 is not considered in excess; add TiO_2 in the list of thermodynamic components; change the P-T range of interest.

(2) Doing the calculation (VERTEX)

Run vertex to make the calculation:

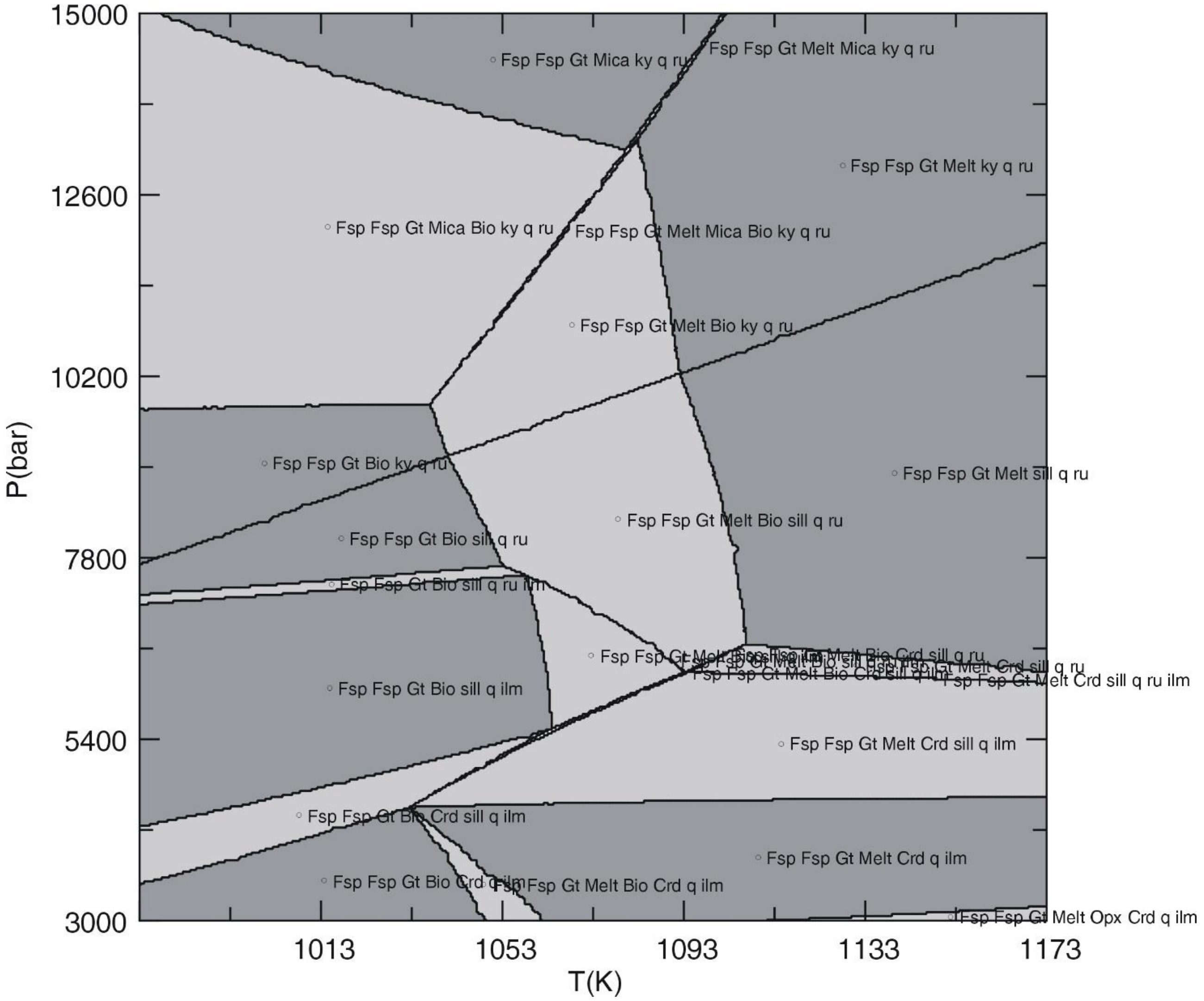
```
C:\PERPLEX\Perplex689>vertex

Perple_X version 6.8.9, source updated Jan 31, 2020.
Copyright (C) 1986-2020 James A D Connolly <www.perplex.ethz/copyright.html>.

Enter the project name (the name assigned in BUILD) [default = my_project]:
Ex13
...
```

(3) Plotting the calculated phase diagram (PSSECT)

Run PSSECT to plot the calculated pseudosection:

```
C:\PERPLEX\Perplex689>pssect

Perple_X version 6.8.9, source updated Jan 31, 2020.
Copyright (C) 1986-2020 James A D Connolly <www.perplex.ethz/copyright.html>.

Enter the project name (the name assigned in BUILD) [default = my_project]:
Ex13
...
```

ex13



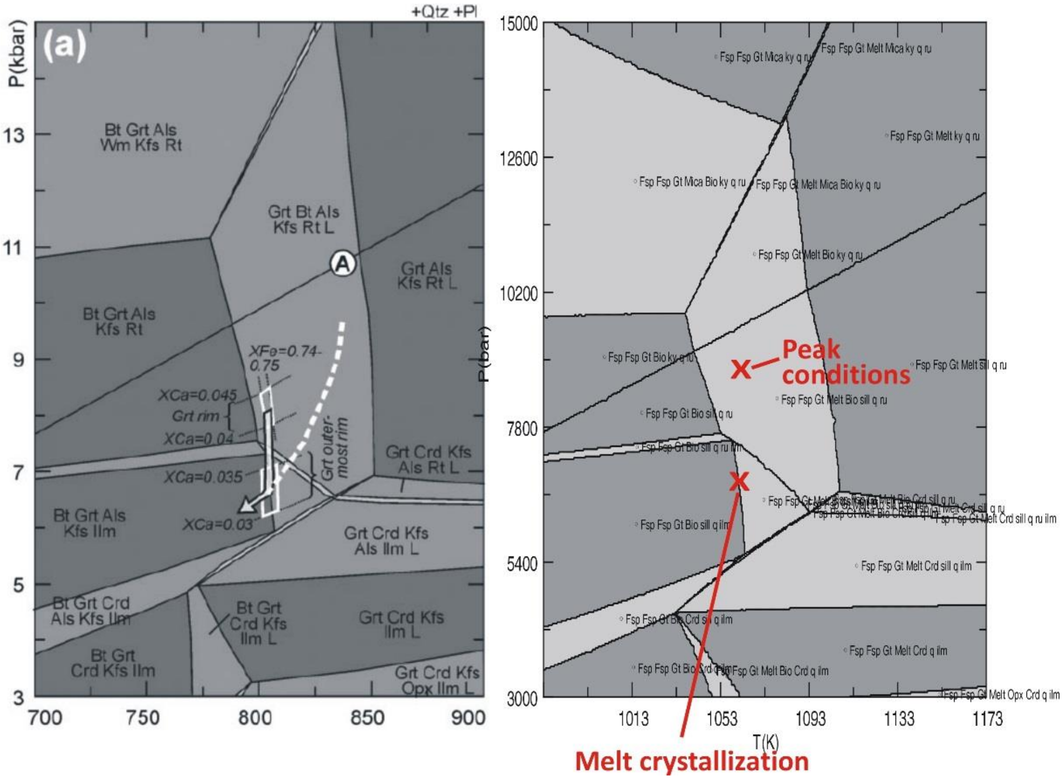
Peak P-T conditions can be derived by:

(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.



Peak conditions

Melt crystallization

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: 790°C, 6 kbar) are comparable (within the error) with the observed mineral modes.

Werami, option 1

```
Stable phases at:
                 T(K)     =  1063.00
                 P(bar)   =  6000.00

Phase Compositions (molar  proportions):
          wt %    vol %   mol %    mol      H2O     Na2O     MgO     Al2O3    K2O      CaO      FeO      TiO2     SiO2
Fsp       14.26   15.20    5.22    3.32    0.00000  0.12463  0.00000  0.51339  0.36198  0.02679  0.00000  0.00000  2.97321
Fsp       14.34   14.85    5.38    3.42    0.00000  0.31723  0.00000  0.64222  0.04055  0.28445  0.00000  0.00000  2.71555
Gt         5.26    3.52    1.12   0.712    0.00000  0.00000  0.74950  1.00000  0.00000  0.06668  2.18381  0.00000  3.00000
Bio        9.49    8.53    2.07    1.32    0.79051  0.00000  1.25154  0.79142  0.50000  0.00000  1.24755  0.20949  2.70858
sill       7.45    6.25    4.62    2.94    0.00000  0.00000  0.00000  1.00000  0.00000  0.00000  0.00000  0.00000  1.00000
q         48.49   51.25   81.13    51.6    0.00000  0.00000  0.00000  0.00000  0.00000  0.00000  0.00000  0.00000  1.00000
ilm        0.70    0.40    0.46   0.294    0.00000  0.00000  0.00000  0.00000  0.00000  0.00000  1.00000  1.00000  0.00000
```

Mineral modes

	790°C, 6 kbar	
	observed	modelled
Qtz	51.7	51.2
Kfs	14.3	15.2
Sil	5.1	6.2
Bt	9.2	8.5
Grt	4.8	3.5
Pl	14.7	14.8

Ex. 13.2 – 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 bulk 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 (790°C, 9.0 kbar)

```
Stable phases at:
                   T(K)    = 1063.00
                   P(bar)  = 9000.00

Phase Compositions (molar  proportions):
          wt %   vol %   mol %    mol     H2O      Na2O     MgO      Al2O3    K2O      CaO      FeO      TiO2     SiO2
Fsp       15.97  17.05   5.92    3.72    0.00000  0.11496  0.00000  0.51265  0.37240  0.02530  0.00000  0.00000  2.97470
Fsp       13.37  13.88   5.08    3.19    0.00000  0.32180  0.00000  0.63616  0.04204  0.27232  0.00000  0.00000  2.72768
Gt         8.89   6.02   1.92    1.21    0.00000  0.00000  0.80531  1.00000  0.00000  0.11489  2.07980  0.00000  3.00000
Melt       1.22   1.51   0.99    0.623   0.56141  0.07226  0.00225  0.17788  0.07362  0.01216  0.00604  0.00000  1.40439
Bio        6.22   5.63   1.38    0.869   0.79423  0.00000  1.38613  0.79026  0.50000  0.00000  1.11784  0.20577  2.70974
sill       6.73   5.67   4.23    2.66    0.00000  0.00000  0.00000  1.00000  0.00000  0.00000  0.00000  0.00000  1.00000
q         47.12  49.93  79.85   50.2     0.00000  0.00000  0.00000  0.00000  0.00000  0.00000  0.00000  0.00000  1.00000
ru         0.49   0.32   0.62    0.391   0.00000  0.00000  0.00000  0.00000  0.00000  0.00000  0.00000  1.00000  0.00000
```

Calculate the re-integrated bulk compositions adding small amounts of melt to the measured bulk composition.

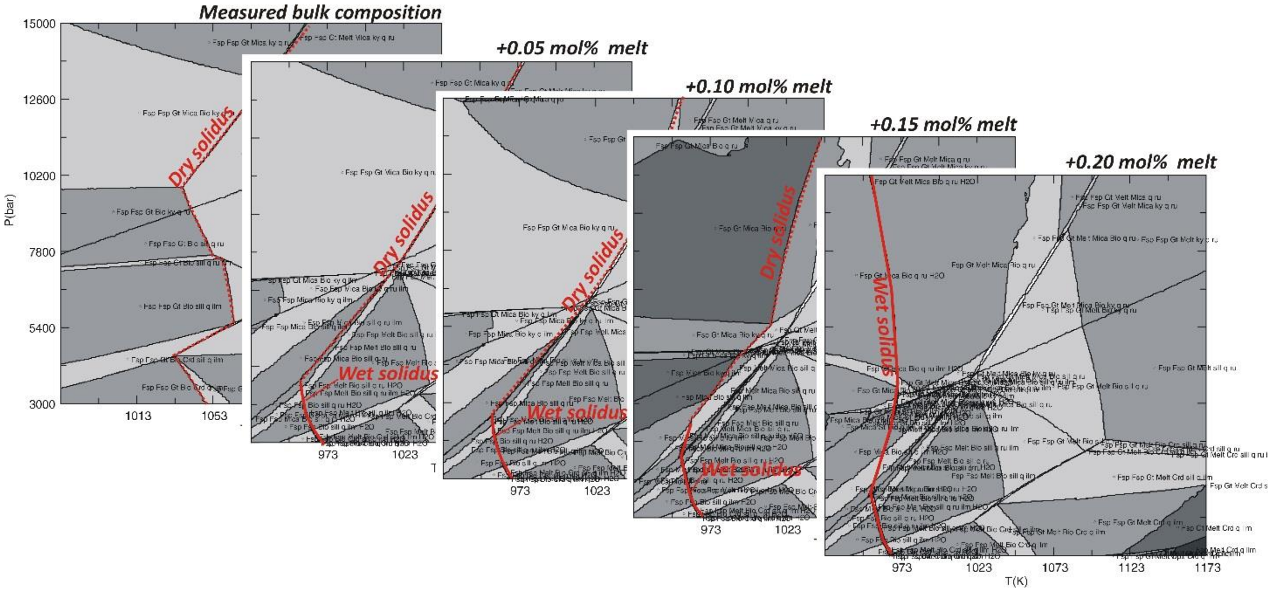
	melt composition (790°C, 9.0 kbar)		BC**	Melt reintegrated bulk compositions							
	mol*	mol%	mol%	+ 0.05 mol%		+ 0.10 mol%		+ 0.15 mol%		+ 0.20 mol%	
SiO2	1.4044	60.80	79.45	82.5	78.56	85.5	77.75	88.6	77.02	91.6	76.34
TiO2	0.0000	0.00	0.57	0.6	0.54	0.6	0.52	0.6	0.50	0.6	0.48
Al2O3	0.1779	7.70	8.60	9.0	8.56	9.4	8.52	9.8	8.48	10.1	8.45
FeO	0.0060	0.26	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	0.0023	0.10	2.18	2.2	2.08	2.2	1.99	2.2	1.91	2.2	1.83
CaO	0.0122	0.53	1.11	1.1	1.08	1.2	1.06	1.2	1.03	1.2	1.01
Na2O	0.0723	3.13	1.50	1.7	1.58	1.8	1.65	2.0	1.71	2.1	1.77
K2O	0.0736	3.19	2.00	2.2	2.06	2.3	2.11	2.5	2.15	2.6	2.20
H2O	0.5614	24.30	1.04	2.3	2.15	3.5	3.15	4.7	4.07	5.9	4.92
Total	2.3100	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).