PERPLE_X TUTORIALS

This set of 15 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 7.1.10** (released on December 21, 2024). 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 15 exercises are as follows:

Understanding the differences between projections, chemographies and pseudosections

Ex 1: P-T projection for the Al_2SiO_5 system Pag. 4

This exercise explains how to calculate a P-T projection 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.

Ex 2: P-T projection for the CMSH system (no solid solutions) Pag. 17

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

Ex 3: Composition diagrams (chemographies) for the CMSH system Pag. 31

This exercise explains how to calculate composition diagrams (i.e. chemographic diagrams) for the P-T projection of Ex. 2, at specified P-T conditions.

Ex 4: P-T isochemical phase diagram for the CMSH system (no solid solutions) Pag. 43

This exercise explains how to calculate a very simple pseudosection, not involving solid solutions. Combined with Ex. 2 and Ex. 3, this exercise is useful to understand the difference between P-T projections and P-T isochemical phase diagrams.

Ex 5: T-X(CO_2) projections and isochemical phase diagrams for the CMS-H_2O-CO_2 system (no solid solutions) Pag. 55

This exercise investigates prograde metamorphism of impure dolomites and limestones characterized by different amounts of Cal, Dol and Qz. 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) isochemical phase diagrams and allows you to become familiar with the use of H_2O-CO_2 fluids.

Working with solid solutions

Ex 6: T-XMg section for the $CaCO_3$-$MgCO_3$ system (solvus relations) Pag. 86

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. 100

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 chemographic diagrams in the KFMASH system Pag. 116

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 isochemical phase diagram for a METAPELITE (KFMASH system) Pag. 131

This exercise explains how to calculate a P-T isochemical phase diagram 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 Perple_X outputs are given, and the comparison with the AFM chemographic diagrams 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 isochemical phase diagram for a METAPELITE (MnNKCFMASH system) Pag. 161

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 section for a METAPELITE (MnNKCFMASH system) Pag. 172

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 section (i.e. a phase diagram section with a compositional parameter on the horizontal axis).

Ex 12: P-T pseudosection for a "real" metapelite and isopleths thermobarometry Pag. 181

This exercise shows how to calculate a P-T pseudosection for a "real" metapelite, with the aim of retrieving the equilibrium P-T conditions of a specific metamorphic stage.

The exercise illustrates how, once that the isochemical phase diagram is modelled, equilibrium P–T conditions can be constrained by comparing the predicted mineral assemblages and compositions with the observed ones. If the observed mineral assemblage and composition reflect equilibrium conditions, the modelled isopleths should intersect (or converge) in a single, narrow, P–T domain. The method is called **"ISOPLETH THERMOBAROMETRY"**. To enhance the interpretation of isopleth thermobarometry, **IntersecT is further applied, which QUANTIFIES the quality of fit between the modelled and the observed composition of the phases** and accounts for uncertainties in the measured mineral compositions.

Modelling a melt-bearing system

Ex 13: DIRECT modelling of an anatectic METAPELITE (NKCFMASH system) Pag. 222

This exercise deals with the "DIRECT" modelling of a metapelite sample at supra-*solidus* conditions (i.e. melt-bearing conditions). "Direct modelling" means that you know which is the protolith composition, including its initial H_2O amount (which is generally not the case).

Ex 14: Modelling melt fractionation (NKCFMASH system) Pag. 243

This exercise illustrates MELT FRACTIONATION CALCULATIONS for the same system investigated in Ex. 12. Melt fractionation is modelled along a defined prograde path. This exercise simulates what is observed in nature, i.e. most migmatites and granulites have lost some to virtually all of their melt during metamorphism.

Ex 15: INDIRECT modelling of an anatectic METAPELITE (NKCFMASTH system) Pag. 256

This exercise explains the strategy for modelling a REAL SAMPLE OF ANATECTIC METAPELITE, i.e. a metapelite whose protolith is unknown, and that has lost some melt during prograde metamorphism. The basic principles of the melt-reintegration approach are discussed.

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\Perplex7110>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]:
```

Here you specify the name of 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 = hp62ver.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 ENTER. 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 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
```

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
6 - 0-d Infiltration-reaction-fractionation
7 - 2-d Phase fractionation (FRAC2D and TITRATE reactive transport models)
8 - (pseudo-)Ternary liquidus/solidus surfaces

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 SiO2 as a saturated component.

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

y

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

Select < 6 saturated components from the set:

NA2O MGO AL2O3 SIO2 K2O CAO TIO2 MNO FEO NIO ZRO2 CL2 O2 H2O CO2

Enter names, 1 per line, press <enter> to finish:
SIO2
(NB. It is CASE-SENSITIVE!).

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

Select thermodynamic components from the set:
NA2O MGO AL2O3 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.

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 models (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\Perplex7110>convex

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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       [auto] manual off
    replicate_threshold     0.1E-1    [1e-2]; static opt; <0 => no replica test
    rep_dynamic_threshold   0.1E-2    [1d-3]; dynamic opt; <0 => no replica test
    re-refine             F         [F] T
```

```
  intermediate_savrpc     F         [F] T
  intermediate_savdyn     F         [F] T
  keep_all_rpcs           T         [T] F
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 [     ], 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:
  P_stop (bar)            0.        [0]
  PT_freeze               F         [T] F
  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]
  approx_alpha            T         [T] F
  Anderson-Gruneisen      F         [F] T
  finite_strain_alpha     F         [F] T
  speciation_precision    0.1E-4    [1d-5] <1; absolute
  speciation_max_it       100       [100]
  function_tolerance_exp  0.8       [0.8] sets x in tol = epsmch^x
  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_lagged_speciation    F         [F] T
  aq_fractionation_simpl  F         [F] T
  aq_ion_H+               T         [T] F => use OH-
  aq_oxide_components     F         [F] T
  aq_solvent_solvus_tol   0.5       [0.5] 0-1
  aq_vapor_epsilon        1.0       [1.]
Input/Output options:
  timing                  T         [T] F
  auto_exclude            T         [T] F
  output_iteration_detai  F         [F] T
  output_iteration_g      F         [F] T
Error/warning control options:
  pause_on_error          T         [T] F
  max_warn_limit          5         [5]
  warn_interactive        T         [T] F
```

```
  aq_error_ver100      F      [F] T, abort during iteration
  aq_error_ver101      T      [T] F, solute undersaturation abort
  aq_error_ver102      T      [T] F, pure + impure solvent abort
  aq_error_ver103      T      [T] F, out-of-range HKF g abort
  aq_error_ver104      T      [T] F, abort on failed respeciation
  warning_ver637       T      [T] F
  error_ver109       T      [T] F
  do_not_reset_options   F      [F] T, prevents automatic resets
To change these options see: www.perplex.ethz.ch/perplex_options.html
```

The calculation starts here:

```
--------------------------------------------------------------------------------
Summary of make-definition entities:
  sil8L   q8L
--------------------------------------------------------------------------------
--------------------------------------------------------------------------------
Summary of saturated-component entities:
 for: SIO2
  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\Perplex7110>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 :
```

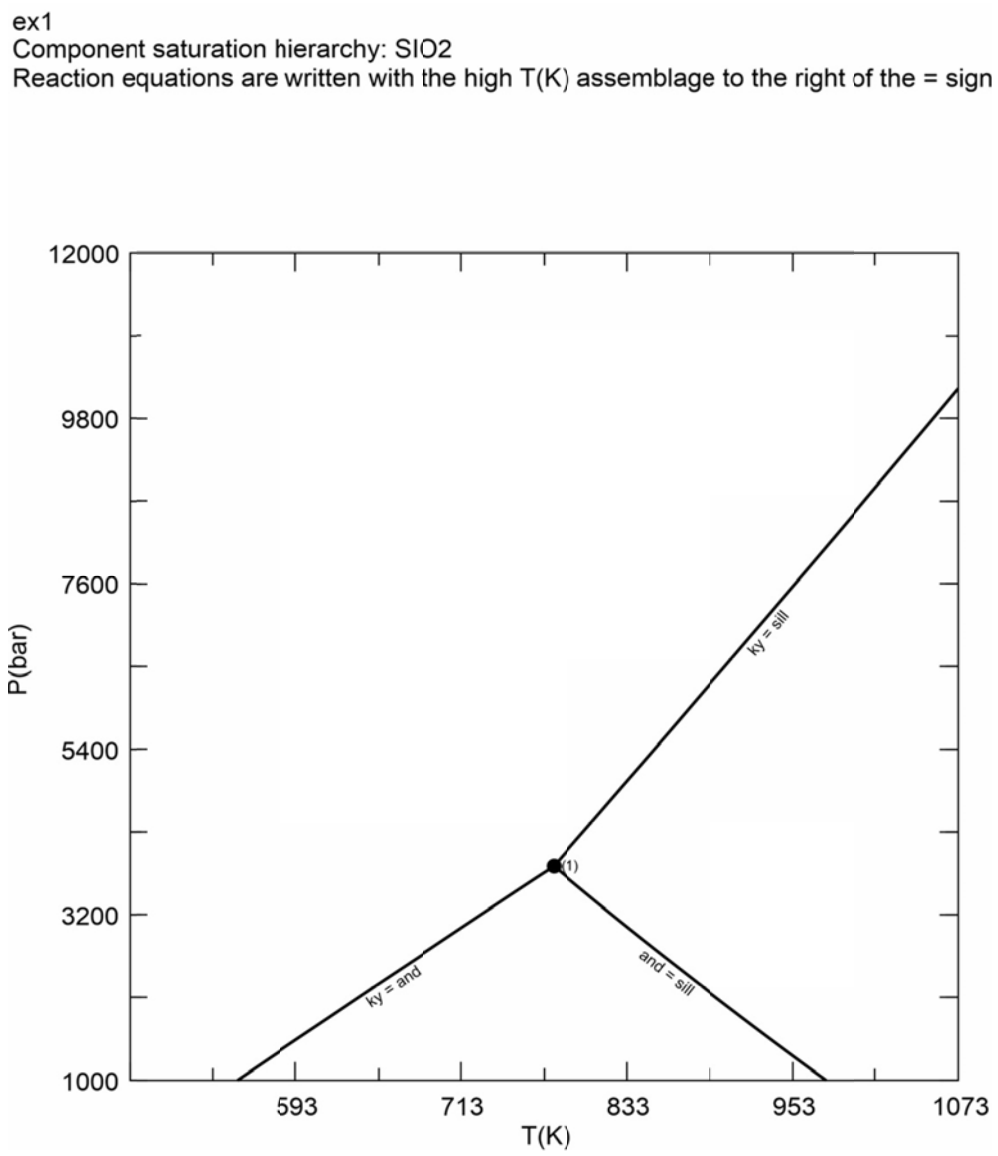
```
                 0     [0] x-min (pts)
                 0     [0] y-min (pts)
               800     [800] x-length (pts)
               800     [800] y-length (pts)
  contour_t_interval      50.00    >0 [50.0]
  contour_p_interval     1000.00    >0 [1000.0]
  field_fill            T         [T] F
  field_label           T         [T] F
  numeric_field_label    F         [F] T, if T PSSECT writes list to *_assemblages.txt
  replicate_label       0.250     0->1 [0.025]
  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
  splines               T         [T] F
  tenth_ticks           F         [F] T
  text_scale            1.000      [1.] (rel)
  plot_extra_data       F         [T] F, to plot, e.g., experimental observations
To change these options edit or create the plot option file See: www.perplex.ethz.ch/perplex_plot_options.html

PostScript will be written to file: ex1.ps

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

If you replay Y to this prompt, you can change the output, for example you can modify the minimum and maximum T or P along the axes etc. (see below).

At the end, you have a new file ex1.ps in the Perple_X folder. You can open this file with any graphical software (e.g. CorelDraw, Adobe Illustrator etc.) and also convert it in a pdf file.



ex1
Component saturation hierarchy: SIO2
Reaction equations are written with the high T(K) assemblage to the right of the = sign

The alumino-silicate triple point is modelled at 507°C, 3.8 kbar.

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

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

Run again PSVDRAW:

```
C:\PERPLEX\Perplex7110>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)
  contour_t_interval      50.00    >0 [50.0]
  contour_p_interval     1000.00    >0 [1000.0]
  field_fill            T         [T] F
  field_label           T         [T] F
  numeric_field_label    F         [F] T, if T PSSECT writes list to *_assemblages.txt
  replicate_label       0.250      0->1 [0.025]
  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
  splines               T         [T] F
  tenth_ticks           F         [F] T
  text_scale            1.000     [1.] (rel)
  plot_extra_data       F         [T] F, to plot, e.g., experimental observations
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:
   - field labeling
   - 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)?

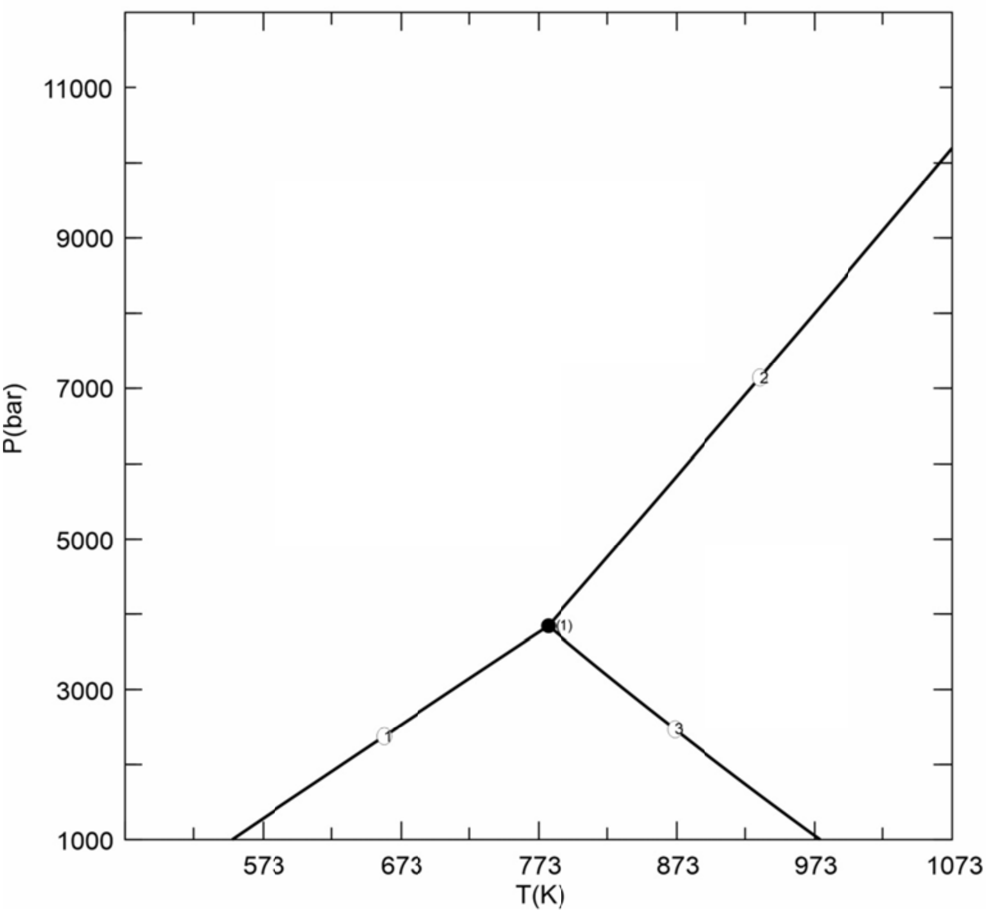
y

Enter the starting value and interval for major tick marks on the X-axis (current values are: 473. 120.)
Enter the new values:

473
100

Enter the starting value and interval for major tick marks on the Y-axis (current values are: 0.100E+04 0.220E+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**.

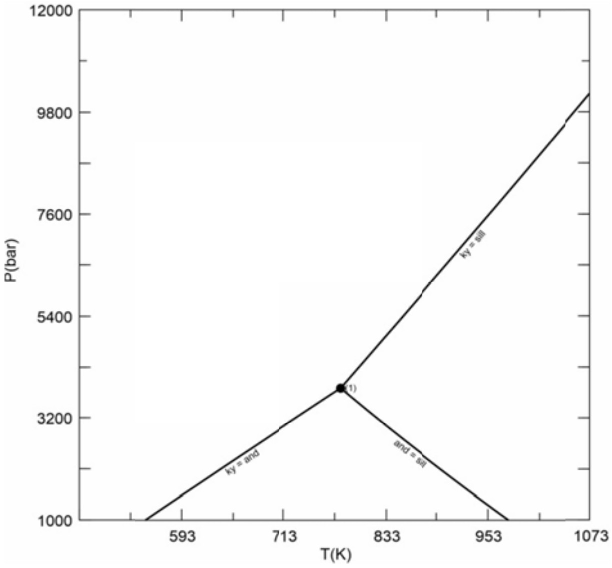
```
hp62ver.dat     thermodynamic data file
```

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.

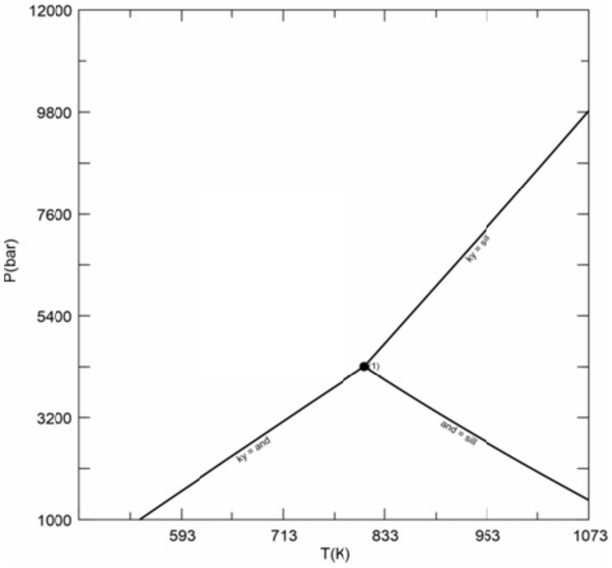
```
begin thermodynamic component list
Al2O3 0  0.00000      0.00000      0.00000     unconstrained amount
end thermodynamic component list

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.



HP02 DATABASE



HP62 DATABASE

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\Perplex7110>build

Perple_X release 7.1.10 Dec 21, 2024.
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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 = hp62ver.dat]:
```

The HP (Holland & Powell) databases are the most used in metamorphic petrology. 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.

```
[ENTER]

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
```

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. $FE_2O_3 = 2FEO + 0.5 O_2$).

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
6 - 0-d Infiltration-reaction-fractionation
7 - 2-d Phase fractionation (FRAC2D and TITRATE reactive transport models)
8 - (pseudo-)Ternary liquidus/solidus surfaces
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.

```
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
```

```
Select the EoS to be used for the saturated fluid constraint:
   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*
  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
  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  - MRK DeSantis et al 1974
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

```
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
```

```
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
```

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 $Ca_3Si_2O_7$
lrn	larnite Ca_2SiO_4
cstn	"Si-titanite" $CaSi_2O_5$ (one Si replaces Ti)
wo	wollastonite $CaSiO_3$
pswo	pseudo-wollastonite $CaSiO_3$
wal	wollastonite $CaSiO_3$
ak	akermanite $Ca_2MgSi_2O_7$
merw	merwinite $Ca_3MgSi_2O_8$
mont	monticellite $CaMgSiO_4$
chum	clinohumite $Mg_9Si_4O_{16}(OH)_2$
cen	clinoenstatite $Mg_2Si_2O_6$
cumm	cummingtonite $Mg_7Si_8O_{22}(OH)_2$
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 models (Y/N)?
n
```

Solid solutions are not considered, 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\Perplex7110>convex

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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: hp62ver.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       [auto] manual off
    replicate_threshold     0.1E-1    [1e-2]; static opt; <0 => no replica test
    rep_dynamic_threshold   0.1E-2    [1d-3]; dynamic opt; <0 => no replica test
    re-refine              F         [F] T
    intermediate_savrpc     F         [F] T
    intermediate_savdyn     F         [F] T
    keep_all_rpcs          T         [T] F

 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 [     ], 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:
    P_stop (bar)           0.        [0]
    PT_freeze              F         [T] F
    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]
    approx_alpha           T         [T] F
    Anderson-Gruneisen     F         [F] T
    finite_strain_alpha    F         [F] T
    speciation_precision   0.1E-4    [1d-5] <1; absolute
    speciation_max_it      100       [100]
```

```
   function_tolerance_exp  0.8      [0.8] sets x in tol = epsmch^x
   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_lagged_speciation   F        [F] T
   aq_fractionation_simpl  F        [F] T
   aq_ion_H+              T        [T] F => use OH-
   aq_oxide_components    F        [F] T
   aq_solvent_solvus_tol  0.5      [0.5] 0-1
   aq_vapor_epsilon       1.0      [1.]

  Input/Output options:
   timing                 T        [T] F
   auto_exclude           T        [T] F
   output_iteration_detai  F        [F] T
   output_iteration_g     F        [F] T

  Error/warning control options:
   pause_on_error         T        [T] F
   max_warn_limit          5       [5]
   warn_interactive       T        [T] F
   aq_error_ver100        F        [F] T, abort during iteration
   aq_error_ver101        T        [T] F, solute undersaturation abort
   aq_error_ver102        T        [T] F, pure + impure solvent abort
   aq_error_ver103        T        [T] F, out-of-range HKF g abort
   aq_error_ver104        T        [T] F, abort on failed respeciation
   warning_ver637         T        [T] F
   error_ver109           T        [T] F
   do_not_reset_options   F        [F] T, prevents automatic resets
To change these options see: www.perplex.ethz.ch/perplex_options.html
--------------------------------------------------------------------------------
Summary of make-definition entities:
   fo8L     q8L     cenjh    odi     qjL     dijL    fojL     foHL     qHL
--------------------------------------------------------------------------------
** 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\Perplex7110>psvdraw
```

```
Perple_X release 7.1.10 Dec 21, 2024.
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```

```
Enter the project or plot file name [i.e., without the .plt suffix]:
ex2
```

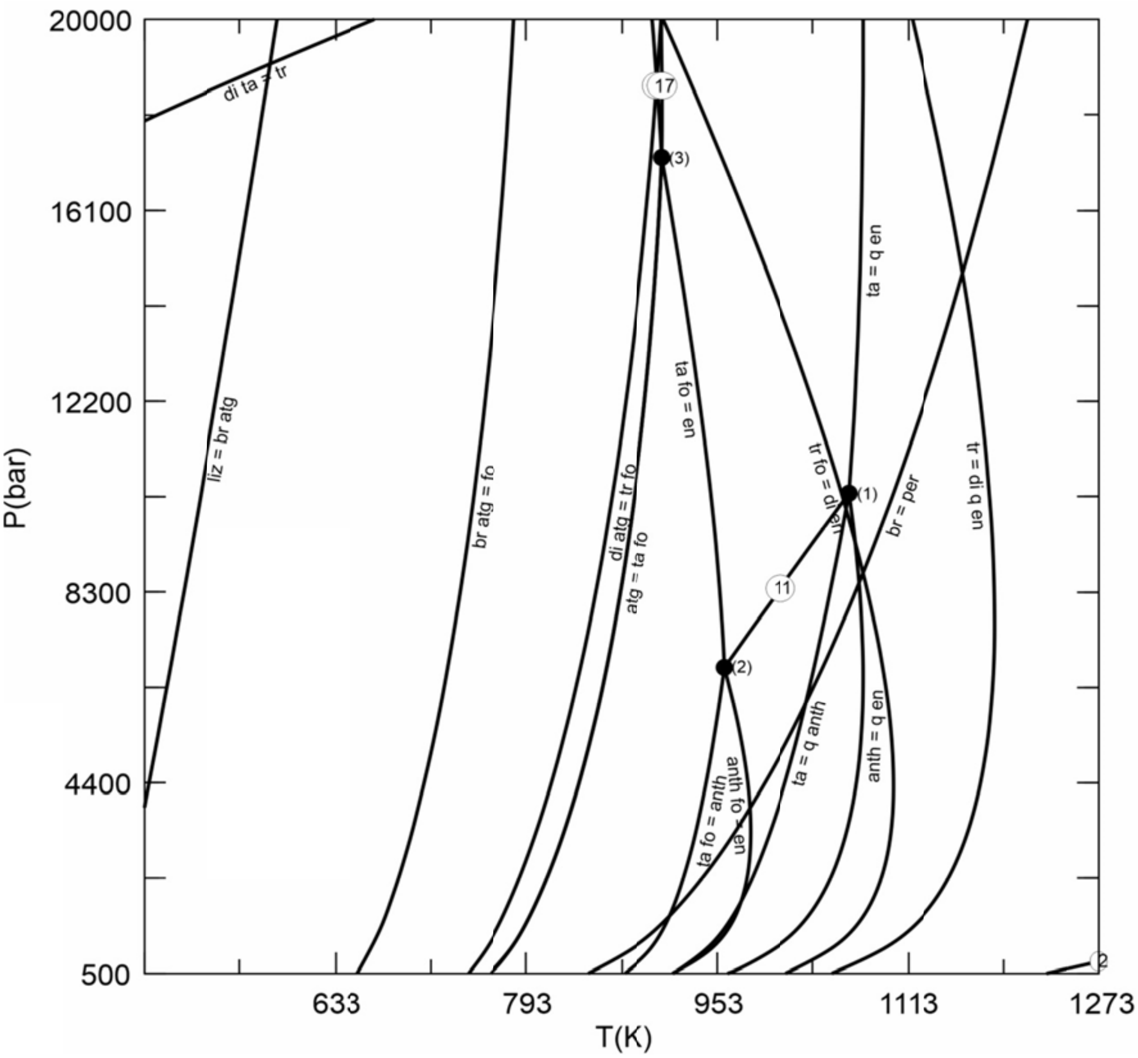
```
Perple_X plot options are currently set as:
   Keyword:              Value:     Permitted values [default]:
   axis_label_scale       1.20       [1.2] (rel)
   bounding_box :
                            0       [0] x-min (pts)
                            0       [0] y-min (pts)
                          800       [800] x-length (pts)
                          800       [800] y-length (pts)
   contour_t_interval       50.00    >0 [50.0]
   contour_p_interval     1000.00    >0 [1000.0]
   field_fill           T          [T] F
   field_label            T          [T] F
   numeric_field_label    F          [F] T, if T PSSECT writes list to *_assemblages.txt
   replicate_label        0.250      0->1 [0.025]
   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
   splines              T         [T] F
   tenth_ticks          F         [F] T
   text_scale           1.000     [1.] (rel)
   plot_extra_data       F        [T] F, to plot, e.g., experimental observations

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 to assign a numeric label (rather than a text label) to (most of) the reaction curves.

Run again PSVDRAW:

```
C:\PERPLEX\Perplex7110>psvdraw

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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)
   contour_t_interval      50.00    >0 [50.0]
   contour_p_interval     1000.00    >0 [1000.0]
   field_fill           T         [T] F
   field_label           T         [T] F
   numeric_field_label    F         [F] T, if T PSSECT writes list to *_assemblages.txt
   replicate_label       0.250      0->1 [0.025]
   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
   splines              T         [T] F
   tenth_ticks           F         [F] T
   text_scale           1.000      [1.] (rel)
   plot_extra_data        F         [T] F, to plot, e.g., experimental observations

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:
- field labeling
- 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.

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

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

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:

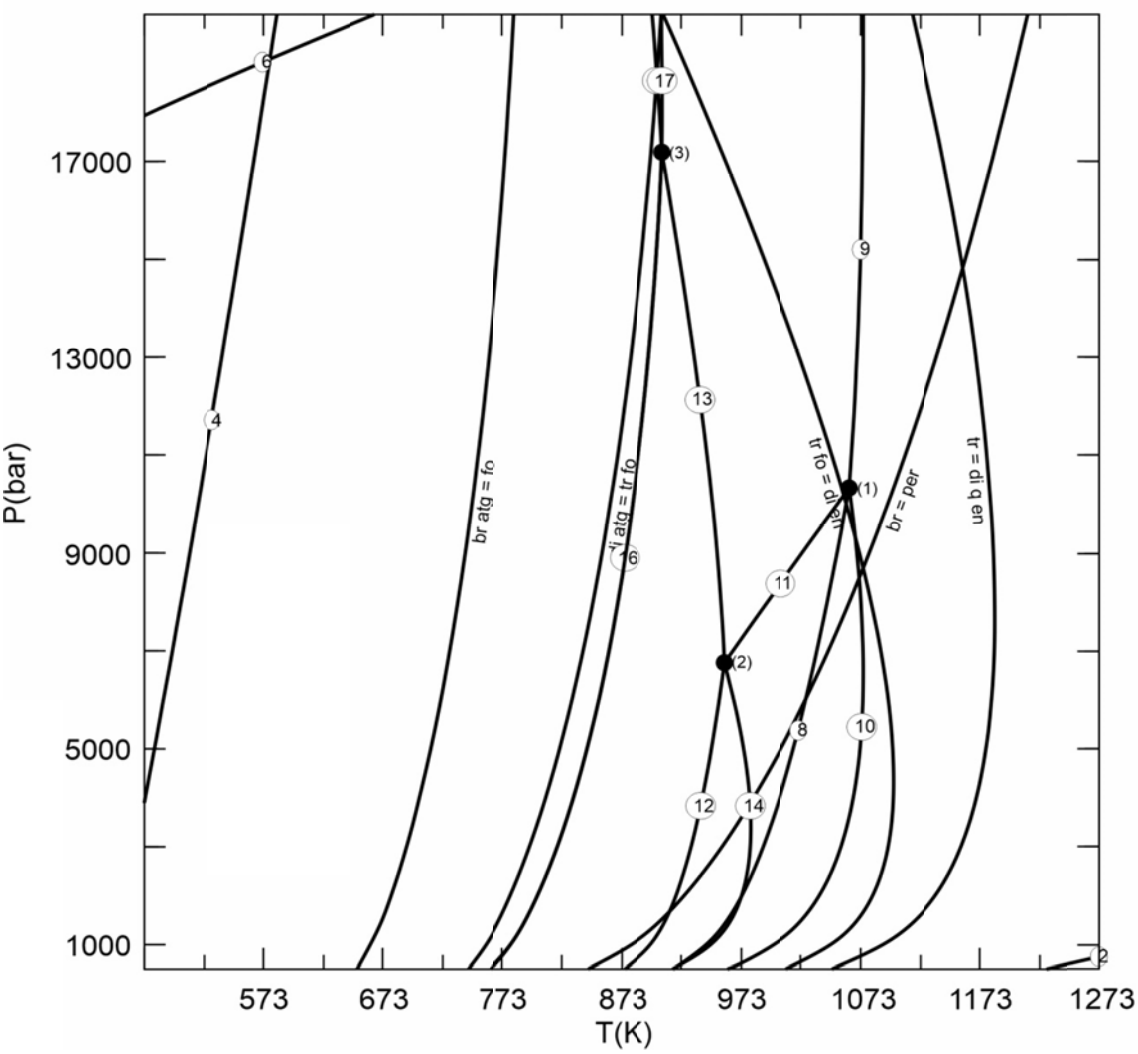
473

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

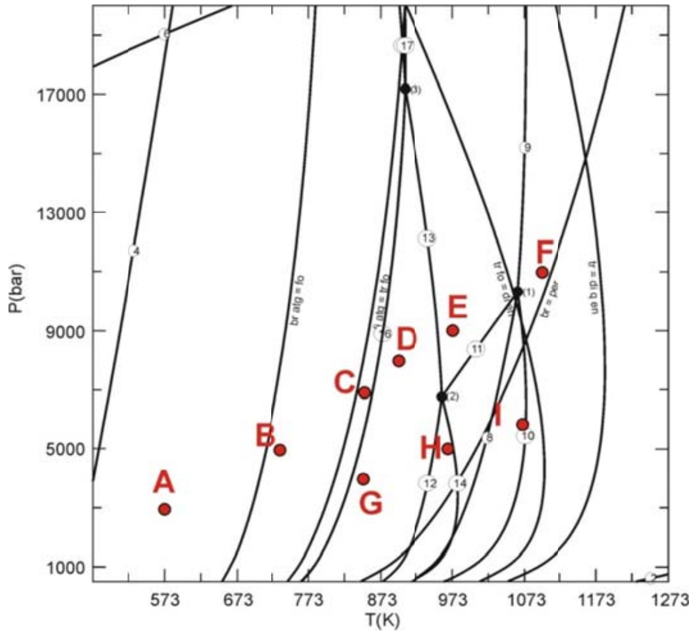


Equilibria corresponding to each reaction number are explained in the ex2.prn file.

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\Perplex7110>build

Perple_X release 7.1.10 Dec 21, 2024.
Copyright (C) 1986-2024 James A D Connolly <www.perplex.ethz.ch/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]:
ex3

The problem definition file will be named: ex3.dat

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

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
    6 - 0-d Infiltration-reaction-fractionation
    7 - 2-d Phase fractionation (FRAC2D and TITRATE reactive transport models)
    8 - (pseudo-)Ternary liquidus/solidus surfaces
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    ZnO
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.

```
Select the EoS to be used for the saturated fluid constraint:
```

```
  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*
 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
 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  - MRK DeSantis et al 1974
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\Perplex7110>convex

Perple_X release 7.1.10 Dec 21, 2024.
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Enter the project name (the name assigned in BUILD) [default = my_project]:
```

ex3

```
Reading problem definition from file: ex3.dat
Reading thermodynamic data from file: hp62ver.dat
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       [auto] manual off
  replicate_threshold     0.1E-1    [1e-2]; static opt; <0 => no replica test
  rep_dynamic_threshold   0.1E-2    [1d-3]; dynamic opt; <0 => no replica test
  re-refine              F         [F] T
  intermediate_savrpc     F         [F] T
  intermediate_savdyn     F         [F] T
  keep_all_rpcs          T         [T] F
 Free energy minimization options:
  MINFRC_diff_increment   0.1E-6    [1e-7] 1e-3 => 1e-9
  MINFXC_solver          0         [0] >= 0 - speci2, -1 - MINFXC
  optimization_max_it     40        [40] >1
  optimization_precision  0.1E-3    [1e-4], 1e-1 => 1e-6, absolute
  dynamic_LP_start       war       [warm] cold hot
  static_LP_start        war       [hot] cold warm
  order_check            F         [F] T
  refinement_points       5         [auto] 1->14
  scatter-points         T         [T] F
  scatter-increment       0.1E-1    [1e-2] 1e-2 => 1e-7
  solvus_tolerance_II     aut       [0.2] 0->1
  zero_mode              0.1E-5    [1e-6] 0->1; < 0 => off
 Solution subdivision options:
  initial_resolution:
   exploratory stage    0.0625     0->1 [1/16], 0 => off
   auto-refine stage    0.0063     0->1 [     ], 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:
  P_stop (bar)           0.        [0]
  PT_freeze              F         [T] F
  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]
  approx_alpha           T         [T] F
  Anderson-Gruneisen      F         [F] T
```

```
    finite_strain_alpha     F        [F] T
    speciation_precision    0.1E-4   [1d-5] <1; absolute
    speciation_max_it       100      [100]
    function_tolerance_exp  0.8      [0.8] sets x in tol = epsmch^x
    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_lagged_speciation    F        [F] T
    aq_fractionation_simpl  F        [F] T
    aq_ion_H+               T        [T] F => use OH-
    aq_oxide_components     F        [F] T
    aq_solvent_solvus_tol   0.5      [0.5] 0-1
    aq_vapor_epsilon        1.0      [1.]
  Input/Output options:
    timing                  T        [T] F
    auto_exclude            T        [T] F
    output_iteration_detai  F        [F] T
    output_iteration_g      F        [F] T
  Error/warning control options:
    pause_on_error          T        [T] F
    max_warn_limit          5        [5]
    warn_interactive        T        [T] F
    aq_error_ver100         F        [F] T, abort during iteration
    aq_error_ver101         T        [T] F, solute undersaturation abort
    aq_error_ver102         T        [T] F, pure + impure solvent abort
    aq_error_ver103         T        [T] F, out-of-range HKF g abort
    aq_error_ver104         T        [T] F, abort on failed respeciation
    warning_ver637          T        [T] F
    error_ver109            T        [T] F
    do_not_reset_options    F        [F] T, prevents automatic resets
To change these options see: www.perplex.ethz.ch/perplex_options.html

--------------------------------------------------------------------------------
Summary of make-definition entities:    fo8L     q8L     cenjh    odi     qjL     dijL
    fojL     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\Perplex7110>psvdraw

Perple_X release 7.1.10 Dec 21, 2024.
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Enter the project or plot file name [i.e., without the .plt suffix]:
ex3
```
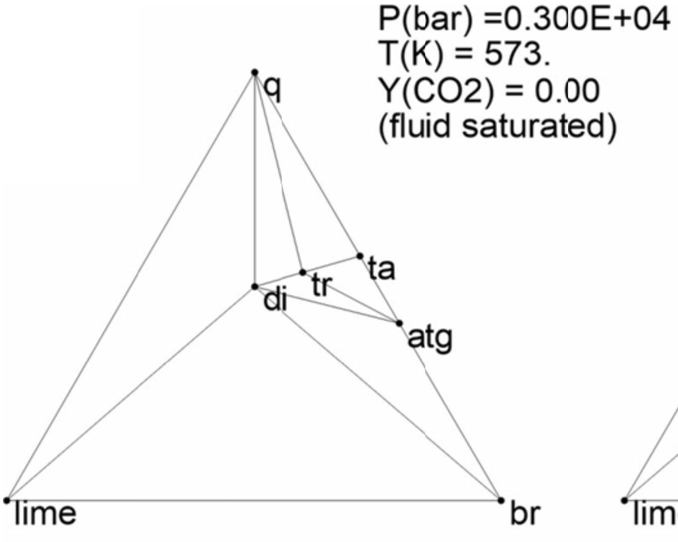
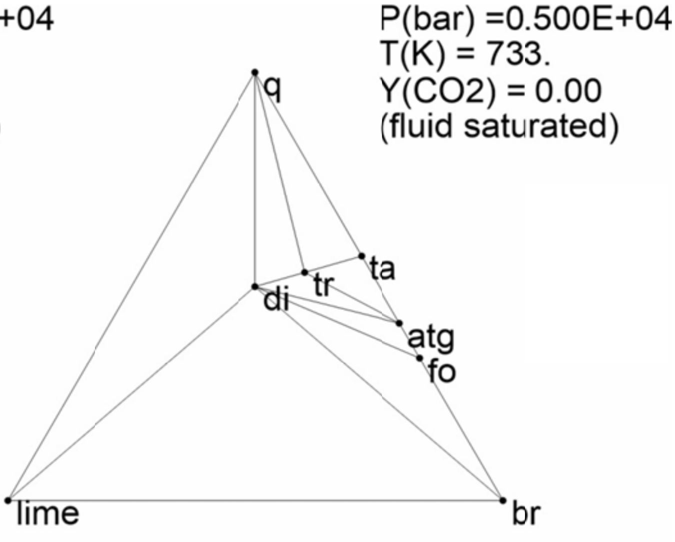
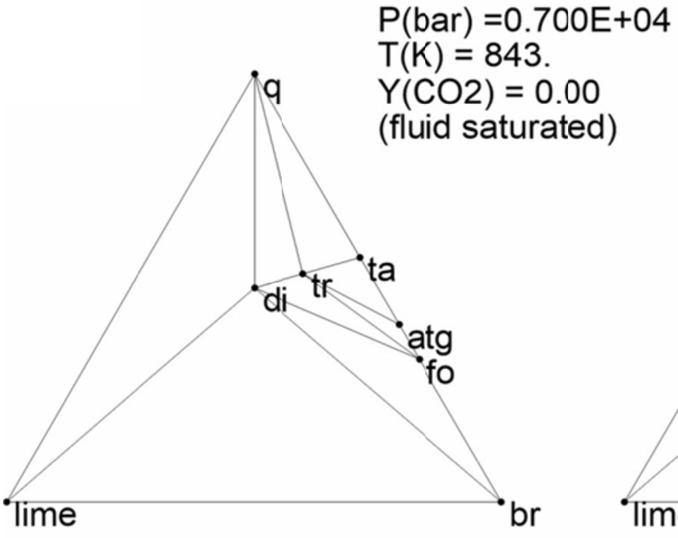
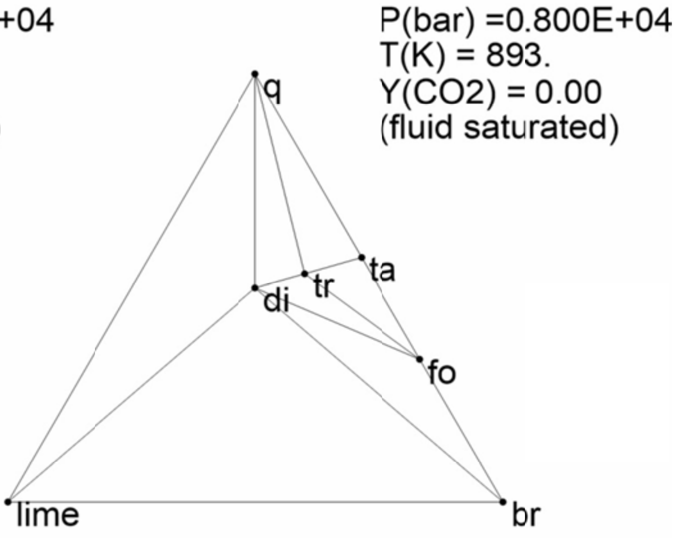
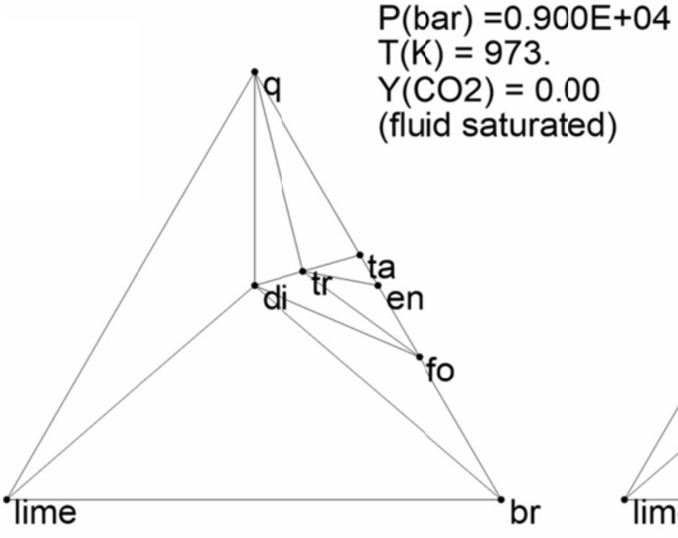

```
Perple_X plot options are currently set as:
   Keyword:            Value:    Permitted values [default]:
   axis_label_scale      1.20      [1.2] (rel)
   bounding_box :
                           0     [0] x-min (pts)
                           0     [0] y-min (pts)
                         800     [800] x-length (pts)
                         800     [800] y-length (pts)
   contour_t_interval      50.00    >0 [50.0]
   contour_p_interval    1000.00    >0 [1000.0]
   field_fill           T        [T] F
   field_label          T        [T] F
   numeric_field_label    F        [F] T, if T PSSECT writes list to *_assemblages.txt
   replicate_label       0.250      0->1 [0.025]
   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
   splines              T        [T] F
   tenth_ticks          F        [F] T
   text_scale           1.000     [1.] (rel)
   plot_extra_data      F        [T] F, to plot, e.g., experimental observations
To change these options edit or create the plot option file See: www.perplex.ethz.ch/perplex_plot_options.html

PostScript will be written to file: ex3.ps

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

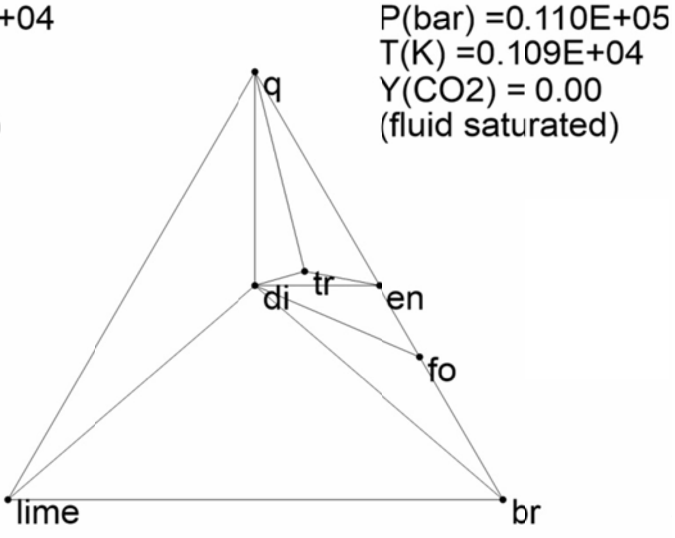

P(bar) =0.300E+04
T(K) = 573.
Y(CO2) = 0.00
(fluid saturated)
q
ta
tr
di
atg
lime
br

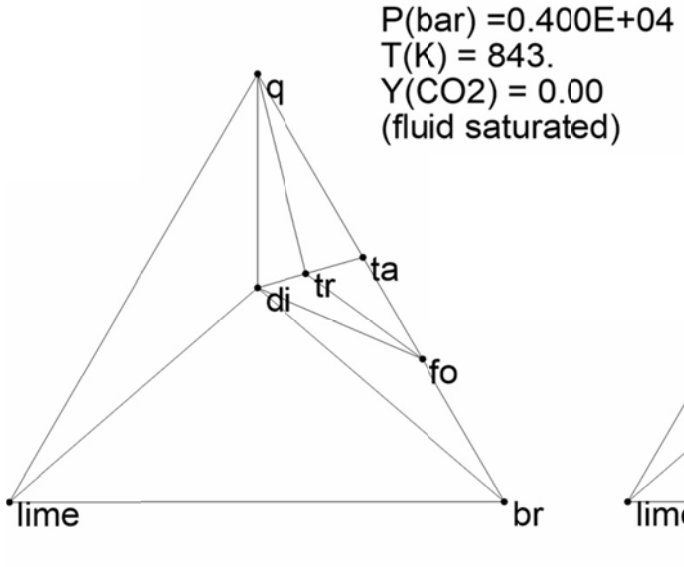

P(bar) =0.500E+04
T(K) = 733.
Y(CO2) = 0.00
(fluid saturated)
q
ta
tr
di
atg
fo
lime
br

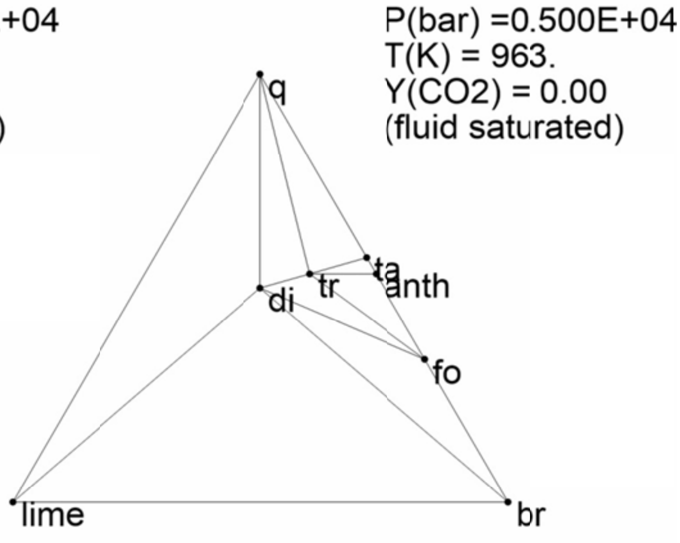

P(bar) =0.700E+04
T(K) = 843.
Y(CO2) = 0.00
(fluid saturated)
q
ta
tr
di
atg
fo
lime
br

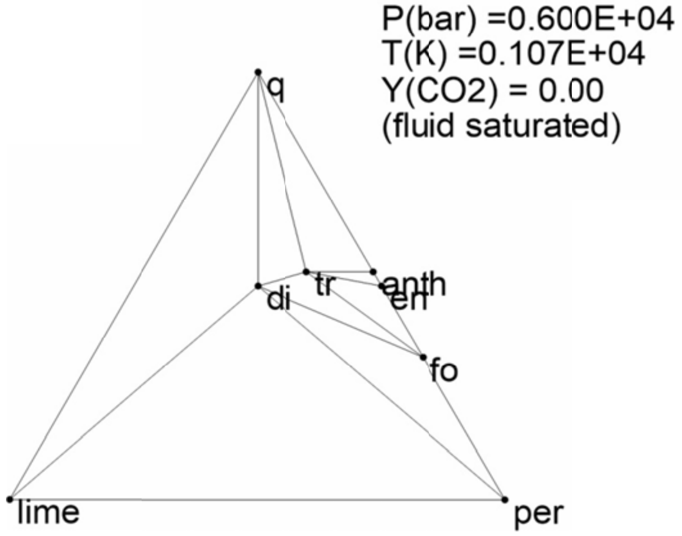

P(bar) =0.800E+04
T(K) = 893.
Y(CO2) = 0.00
(fluid saturated)
q
ta
tr
di
fo
lime
br


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


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


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

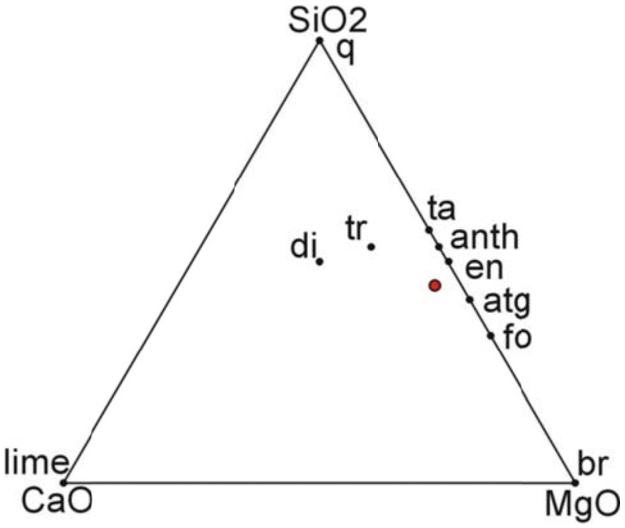

P(bar) =0.500E+04
T(K) = 963.
Y(CO2) = 0.00
(fluid saturated)
q
ta
anth
tr
di
fo
lime
br


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 phase assemblage diagram (pseudosection) for the CMSH system (no solid solutions)

This exercise explains how to calculate a very simple phase assemblage diagram (i.e., 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\Perplex7110>build

Perple_X release 7.1.10 Dec 21, 2024.
Copyright (C) 1986-2024 James A D Connolly <www.perplex.ethz.ch/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 theroot for all output file names) [default = my_project]:
ex4

The problem definition file will be named: ex4.dat

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

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
    6 - 0-d Infiltration-reaction-fractionation
    7 - 2-d Phase fractionation (FRAC2D and TITRATE reactive transport models)
    8 - (pseudo-)Ternary liquidus/solidus surfaces
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
```

```
Select the EoS to be used for the saturated fluid constraint:
   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*
  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
  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  - MRK DeSantis et al 1974
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         20      20        20 x  20 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 chemographic diagrams.

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 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 models (Y/N)?
n

Enter calculation title:
ex4
```

(2) Doing the calculation (VERTEX)

Run VERTEX to make the calculation:

```
C:\PERPLEX\Perplex7110>vertex

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Enter the project name (the name assigned in BUILD) [default = my_project]:
ex4

Reading problem definition from file: ex4.dat
Reading thermodynamic data from file: hp62ver.dat
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      [auto] manual off
    replicate_threshold     0.1E-1    [1e-2]; static opt; <0 => no replica test
    rep_dynamic_threshold   0.1E-2    [1d-3]; dynamic opt; <0 => no replica test
    re-refine             F         [F] T
    intermediate_savrpc     F         [F] T
    intermediate_savdyn     F         [F] T
    keep_all_rpcs          T         [T] F
  Free energy minimization options:
```

```
 MINFRC_diff_increment   0.1E-6    [1e-7] 1e-3 => 1e-9
 MINFXC_solver           0       [0] >= 0 - speci2, -1 - MINFXC
 optimization_max_it     40       [40] >1
 optimization_precision  0.1E-3    [1e-4], 1e-1 => 1e-6, absolute
 dynamic_LP_start       war      [warm] cold hot
 static_LP_start        war      [hot] cold warm
 order_check            F        [F] T
 refinement_points       5       [auto] 1->14
 scatter-points         T        [T] F
 scatter-increment      0.1E-1    [1e-2] 1e-2 => 1e-7
 solvus_tolerance_II     aut      [0.2] 0->1
 zero_mode              0.1E-5    [1e-6] 0->1; < 0 => off
2D grid options:
 x_nodes                20 / 40   [20/40] >0, <2048; effective x-resolution   20 / 313 nodes
 y_nodes                20 / 40   [20/40] >0, <2048; effective y-resolution   20 / 313 nodes
 grid_levels            1 / 4     [1/4] >0, <10
 linear_model           on       [on] off
Solution subdivision options:
 initial_resolution:     0.2000    [1/5] 0->1; 0 => off
 stretch_factor         0.0020    [2d-3] >0
 non_linear_switch       F        [F] T
 subdivision_override    off       [lin] off str
 refine_endmembers       F        [F] T
Thermodynamic options:
 P_stop (bar)           0.       [0]
 PT_freeze              F        [T] F
 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]
 approx_alpha           T        [T] F
 Anderson-Gruneisen      F        [F] T
 finite_strain_alpha     F        [F] T
 speciation_precision    0.1E-4    [1d-5] <1; absolute
 speciation_max_it       100       [100]
 function_tolerance_exp  0.8       [0.8] sets x in tol = epsmch^x
 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_lagged_speciation    F        [F] T
 aq_fractionation_simpl  F        [F] T
 aq_ion_H+              T        [T] F => use OH-
 aq_oxide_components     F        [F] T
 aq_solvent_solvus_tol   0.5       [0.5] 0-1
 aq_vapor_epsilon        1.0       [1.]
Input/Output options:
 timing                 T        [T] F
 auto_exclude           T        [T] F
 output_iteration_detai  F        [F] T
 output_iteration_g      F        [F] T
 logarithmic_p           F        [F] T
 logarithmic_X           F        [F] T
```

```
    bad_number              NaN       [NaN]
    interim_results         aut       [auto] off manual
  Information file output options:
    option_list_files       F         [F] T; echo computational options
    pseudocompound_file     F         [F] T; echo static pseudocompound compositions
    auto_refine_file        F         [T] F; echo auto-refine compositions
    seismic_data_file       T         [F] T; echo seismic wavespeed options
  Error/warning control options:
    pause_on_error          T         [T] F
    max_warn_limit           5        [5]
    warn_interactive        T         [T] F
    aq_error_ver100         F         [F] T, abort during iteration
    aq_error_ver101         T         [T] F, solute undersaturation abort
    aq_error_ver102         T         [T] F, pure + impure solvent abort
    aq_error_ver103         T         [T] F, out-of-range HKF g abort
    aq_error_ver104         T         [T] F, abort on failed respeciation
    warning_ver637          T         [T] F
    error_ver109            T         [T] F
    do_not_reset_options    F         [F] T, prevents automatic resets
To change these options see: www.perplex.ethz.ch/perplex_options.html
--------------------------------------------------------------------------------
Summary of make-definition entities:
    fo8L     q8L     cenjh    odi      qjL      dijL    fojL     foHL     qHL
--------------------------------------------------------------------------------
**warning ver099** no data for aqueous species, aq_output and aq_lagged_speciation disabled.

** Starting exploratory computational stage **
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
--------------------------------------------------------------------------------
Exploratory stage generated:
Total number of compositions:       0
--------------------------------------------------------------------------------
--------------------------------------------------------------------------------
** Starting auto-refine computational stage **
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
-----------------------------------------------------------------------------
    Timing                  min.        % of total
 Static G calculation      0.10417E-02        7.4
 Dynamic G calculation      0.0000           0.0
 Static LP                 0.52083E-03       3.7
 Dynamic LP                 0.0000           0.0
 Successive QP              0.0000           0.0
 Total of above             0.15625E-02       11.1
 Total elapsed time         0.14063E-01      100.0
-----------------------------------------------------------------------------
End of job: ex4
```

(3) Plotting the calculated phase diagram (PSSECT)

Run PSSECT to plot the calculated pseudosection:

```
C:\PERPLEX\Perplex7110>pssect

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Enter the project name (the name assigned in BUILD) [default = my_project]:
ex4

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)
   contour_t_interval      50.00    >0 [50.0]
```
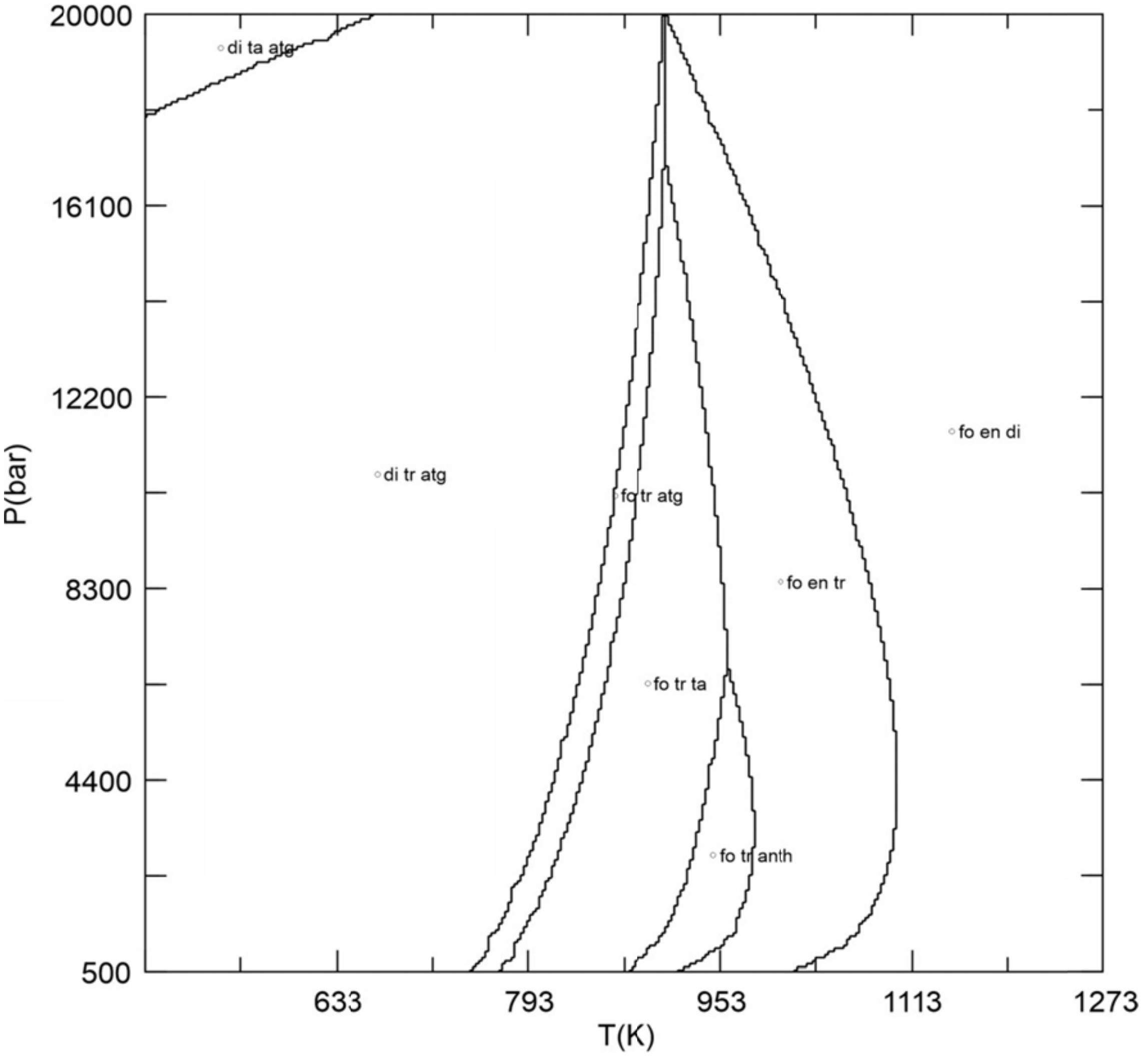
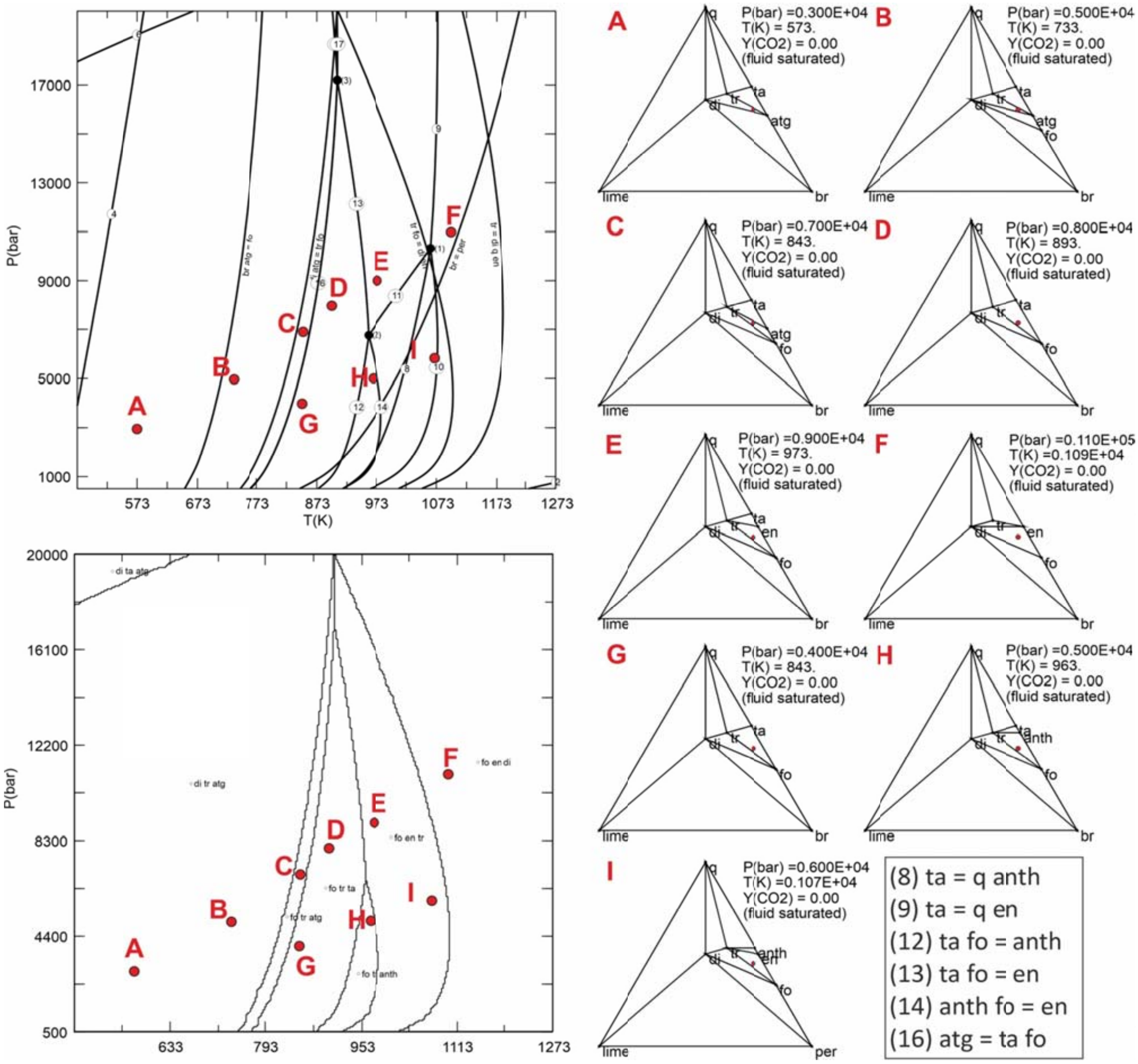

```
  contour_p_interval    1000.00    >0 [1000.0]
  field_fill           T        [T] F
  field_label          T        [T] F
  numeric_field_label    F        [F] T, if T PSSECT writes list to *_assemblages.txt
  replicate_label       0.250      0->1 [0.025]
  field_label_scale      0.75      [0.72] (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
  splines              T        [T] F
  tenth_ticks          F        [F] T
  text_scale           1.000     [1.] (rel)
  plot_extra_data       F        [T] F, to plot, e.g., experimental observations
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 phase assemblage diagram (no solid solutions!), the stability fields of each mineral assemblage are separated by "real" reaction curves, i.e. UNIVARIANT CURVES, and all the field assemblages have the same variance. However, this is a very special case: pseudosections generally contain multi-variant field assemblages.

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

(4) Comparison between projection and pseudosection



Comparison between the CMSH projection (Ex. 2) and the phase assemblage diagram (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 Qz. 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\Perplex7110>build

Perple_X release 7.1.10 Dec 21, 2024.
Copyright (C) 1986-2024 James A D Connolly <www.perplex.ethz.ch/copyright.html>.

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

Enter a name for this project (the name will be used as the root for all output file names) [default = my_project]:
ex5_1

The problem definition file will be named: ex5_1.dat

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

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
    6 - 0-d Infiltration-reaction-fractionation
    7 - 2-d Phase fractionation (FRAC2D and TITRATE reactive transport models)
    8 - (pseudo-)Ternary liquidus/solidus surfaces
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 heirarchy 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

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*
 14 - X(CO2) H2O-CO2 Pitzer & Sterner 94; Holland & Powell mixing 03
 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
 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  - MRK DeSantis et al 1974
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 models (Y/N)?
n

Enter calculation title:
ex5_1
```

(2) Doing the calculation (CONVEX)

Run CONVEX to make the calculation:

```
C:\PERPLEX\Perplex7110>convex

Perple_X release 7.1.10 Dec 21, 2024.
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Enter the project name (the name assigned in BUILD) [default = my_project]:
ex5_1

Reading problem definition from file: ex5_1.dat
Reading thermodynamic data from file: hp62ver.dat
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      [auto] manual off
  replicate_threshold    0.1E-1    [1e-2]; static opt; <0 => no replica test
  rep_dynamic_threshold   0.1E-2    [1d-3]; dynamic opt; <0 => no replica test
  re-refine             F        [F] T
  intermediate_savrpc    F        [F] T
  intermediate_savdyn    F        [F] T
  keep_all_rpcs         T        [T] F
 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 [     ], 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:
  P_stop (bar)           0.       [0]
  PT_freeze             F        [T] F
  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]
  approx_alpha           T        [T] F
  Anderson-Gruneisen     F        [F] T
  finite_strain_alpha    F        [F] T
  speciation_precision    0.1E-4    [1d-5] <1; absolute
  speciation_max_it       100       [100]
  function_tolerance_exp  0.8       [0.8] sets x in tol = epsmch^x
  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_lagged_speciation    F        [F] T
  aq_fractionation_simpl  F        [F] T
  aq_ion_H+             T        [T] F => use OH-
```

```
   aq_oxide_components     F        [F] T
   aq_solvent_solvus_tol   0.5      [0.5] 0-1
   aq_vapor_epsilon        1.0      [1.]
  Input/Output options:
   timing                  T        [T] F
   auto_exclude            T        [T] F
   output_iteration_detai  F        [F] T
   output_iteration_g      F        [F] T
  Error/warning control options:
   pause_on_error          T        [T] F
   max_warn_limit          5        [5]
   warn_interactive        T        [T] F
   aq_error_ver100         F        [F] T, abort during iteration
   aq_error_ver101         T        [T] F, solute undersaturation abort
   aq_error_ver102         T        [T] F, pure + impure solvent abort
   aq_error_ver103         T        [T] F, out-of-range HKF g abort
   aq_error_ver104         T        [T] F, abort on failed respeciation
   warning_ver637          T        [T] F
   error_ver109            T        [T] F
   do_not_reset_options    F        [F] T, prevents automatic resets
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     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
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
finished with equilibrium (     6) di br = fo
finished with equilibrium (     7) fo = wo br

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

finished with equilibrium (     8) atg = di fo
finished with equilibrium (     8) atg = di fo
finished with equilibrium (     9) atg = di br

**warning ver047** univariant field     10 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 (    10) br atg = fo

**warning ver047** univariant field       10 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 (    10) br atg = fo

**warning ver047** univariant field       10 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 (    10) br atg = fo
finished with equilibrium (    10) br atg = fo
finished with equilibrium (    11) tr = di fo
finished with equilibrium (     2) tr = di atg

**warning ver047** univariant field       12 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 (    12) atg = fo tr
finished with equilibrium (    12) atg = fo tr
finished with equilibrium (     1) dol = br
finished with equilibrium (    13) atg dol = fo
finished with equilibrium (     1) dol = br
finished with equilibrium (    14) di dol = fo
finished with equilibrium (    15) tr = di dol
finished with equilibrium (    16) tr dol = fo
finished with equilibrium (    17) tr dol = atg
**warning ver020** sfol2
finished with equilibrium (    18) tr q = di
finished with equilibrium (    19) dol q = di
finished with equilibrium (    20) dol q = tr
finished with equilibrium (    21) ta = atg tr
finished with equilibrium (    22) dol ta = atg
finished with equilibrium (    23) ta = tr dol
finished with equilibrium (    24) q ta = tr
finished with equilibrium (    25) dol q = ta
```

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

Testing divariant assemblage     4,     4 assemblages remaining to be tested.
Testing divariant assemblage     5,     4 assemblages remaining to be tested.
finished with equilibrium (    18) tr q = di
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.
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.
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\Perplex7110>psvdraw

Perple_X release 7.1.10 Dec 21, 2024.
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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:
```
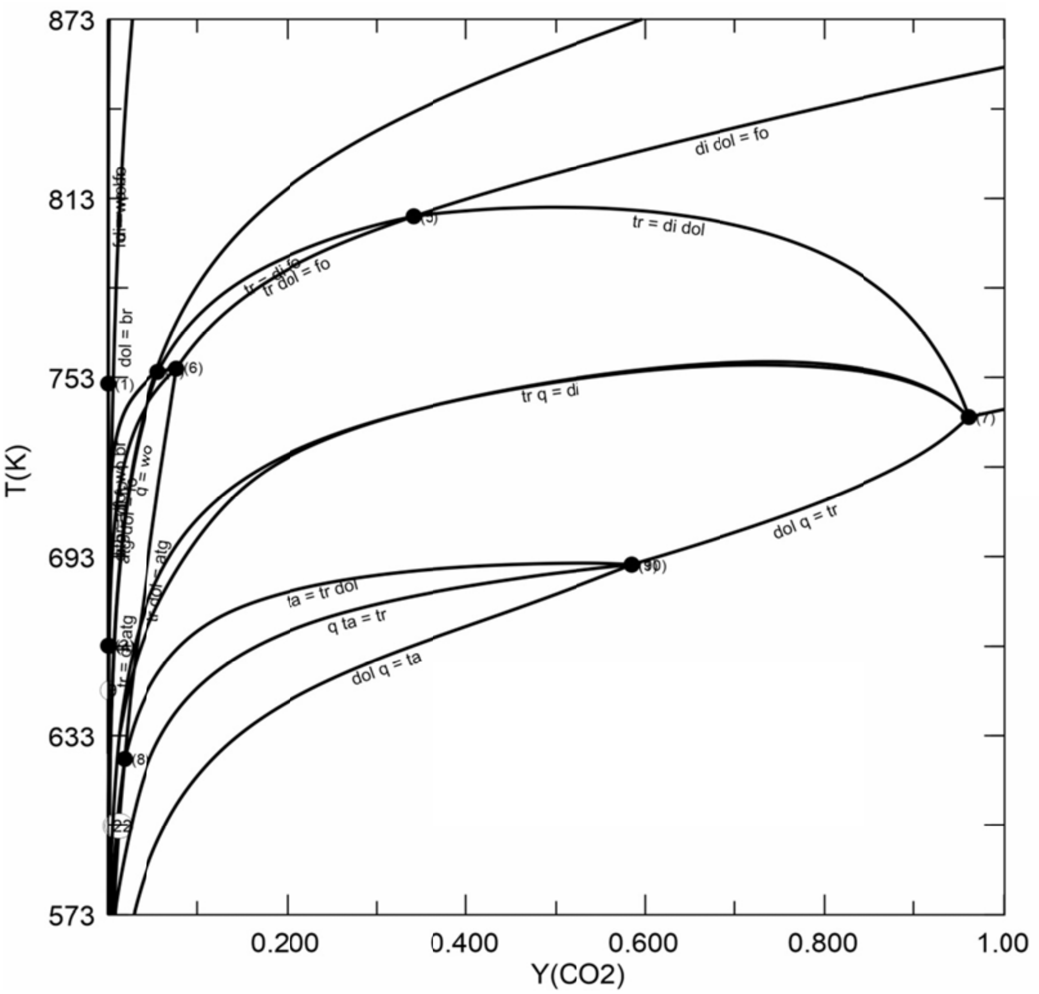

```
   Keyword:            Value:    Permitted values [default]:
   axis_label_scale      1.20      [1.2] (rel)
   bounding_box :
                         0      [0] x-min (pts)
                         0      [0] y-min (pts)
                        800     [800] x-length (pts)
                        800     [800] y-length (pts)
   contour_t_interval      50.00    >0 [50.0]
   contour_p_interval    1000.00    >0 [1000.0]
   field_fill           T        [T] F
   field_label           T        [T] F
   numeric_field_label    F        [F] T, if T PSSECT writes list to *_assemblages.txt
   replicate_label       0.250      0->1 [0.025]
   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
   splines              T        [T] F
   tenth_ticks           F        [F] T
   text_scale           1.000     [1.] (rel)
   plot_extra_data       F        [T] F, to plot, e.g., experimental observations
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)?
N
```



Ex. 5.2 – Isobaric T-XCO_2 pseudosection of a siliceous dolomite for the composition 2Qz–2Dol–1Cal (see Bucher & Grapes, 2011; Fig. 6.8)

(1) Definition of the problem (BUILD)

```
C:\PERPLEX\Perplex7110>build

Perple_X release 7.1.10 Dec 21, 2024.
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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 = hp62ver.dat]:
enter
```

```
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  l2  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
    6 - 0-d Infiltration-reaction-fractionation
    7 - 2-d Phase fractionation (FRAC2D and TITRATE reactive transport models)
    8 - (pseudo-)Ternary liquidus/solidus surfaces
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
```

```
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*
  14 - X(CO2) H2O-CO2 Pitzer & Sterner 94; Holland & Powell mixing 03
  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
  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  - MRK DeSantis et al 1974
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          20      20        20 x  20 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 2Qz +2Dol + 1Cal means: $2SiO_2 + 2MgO + 3CaO$

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 $Ca_3Si_2O_7$
lrn | larnite Ca_2SiO_4
cstn | “Si-titanite” $CaSi_2O_5$ (one Si replaces Ti)
ty | tilleyte $Ca_5Si_2O_7(CO_3)_2$
spu | spurrite $Ca_5Si_2O_8(CO_3)$
ak | akermanite $Ca_2MgSi_2O_7$
merw | merwinite $Ca_3MgSi_2O_8$
mont | monticellite $CaMgSiO_4$
chum | clinohumite $Mg_9Si_4O_{16}(OH)_2$
cen | clinoenstatite $Mg_2Si_2O_6$

Include solution models (Y/N)?
n

```
Enter calculation title:
ex5_2
```

(2) Doing the calculation (VERTEX)

Run VERTEX to make the calculation:

```
C:\PERPLEX\Perplex7110>vertex

Perple_X release 7.1.10 Dec 21, 2024.
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Enter the project name (the name assigned in BUILD) [default = my_project]:
ex5_2

Reading problem definition from file: ex5_2.dat
Reading thermodynamic data from file: hp62ver.dat
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        [auto] manual off
   replicate_threshold   0.1E-1     [1e-2]; static opt; <0 => no replica test
   rep_dynamic_threshold 0.1E-2     [1d-3]; dynamic opt; <0 => no replica test
   re-refine             F          [F] T
   intermediate_savrpc   F          [F] T
   intermediate_savdyn   F          [F] T
   keep_all_rpcs         T          [T] F
 Free energy minimization options:
   MINFRC_diff_increment 0.1E-6     [1e-7] 1e-3 => 1e-9
   MINFXC_solver         0          [0] >= 0 - speci2, -1 - MINFXC
   optimization_max_it   40         [40] >1
   optimization_precision 0.1E-3    [1e-4], 1e-1 => 1e-6, absolute
   dynamic_LP_start      war        [warm] cold hot
   static_LP_start       war        [hot] cold warm
   order_check           F          [F] T
   refinement_points     5          [auto] 1->14
   scatter-points        T          [T] F
   scatter-increment     0.1E-1     [1e-2] 1e-2 => 1e-7
   solvus_tolerance_II   aut        [0.2] 0->1
   zero_mode             0.1E-5     [1e-6] 0->1; < 0 => off
 2D grid options:
   x_nodes               20 / 40    [20/40] >0, <2048; effective x-resolution   20 / 313 nodes
   y_nodes               20 / 40    [20/40] >0, <2048; effective y-resolution   20 / 313 nodes
```

```
  grid_levels           1 / 4     [1/4] >0, <10
  linear_model          on        [on] off
Solution subdivision options:
  initial_resolution:     0.2000    [1/5] 0->1; 0 => off
  stretch_factor         0.0020    [2d-3] >0
  non_linear_switch       F         [F] T
  subdivision_override    off       [lin] off str
  refine_endmembers       F         [F] T
Thermodynamic options:
  P_stop (bar)            0.        [0]
  PT_freeze              F         [T] F
  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]
  approx_alpha            T         [T] F
  Anderson-Gruneisen      F         [F] T
  finite_strain_alpha     F         [F] T
  speciation_precision    0.1E-4    [1d-5] <1; absolute
  speciation_max_it       100       [100]
  function_tolerance_exp  0.8       [0.8] sets x in tol = epsmch^x
  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_lagged_speciation    F         [F] T
  aq_fractionation_simpl  F         [F] T
  aq_ion_H+              T         [T] F => use OH-
  aq_oxide_components     F         [F] T
  aq_solvent_solvus_tol   0.5       [0.5] 0-1
  aq_vapor_epsilon        1.0       [1.]
Input/Output options:
  timing                 T         [T] F
  auto_exclude            T         [T] F
  output_iteration_detai  F         [F] T
  output_iteration_g      F         [F] T
  logarithmic_p           F         [F] T
  logarithmic_X           F         [F] T
  bad_number              NaN       [NaN]
  interim_results         aut       [auto] off manual
Information file output options:
  option_list_files       F         [F] T; echo computational options
  pseudocompound_file     F         [F] T; echo static pseudocompound compositions
  auto_refine_file        F         [T] F; echo auto-refine compositions
  seismic_data_file       T         [F] T; echo seismic wavespeed options
Error/warning control options:
  pause_on_error          T         [T] F
  max_warn_limit          5         [5]
  warn_interactive        T         [T] F
  aq_error_ver100         F         [F] T, abort during iteration
  aq_error_ver101         T         [T] F, solute undersaturation abort
  aq_error_ver102         T         [T] F, pure + impure solvent abort
  aq_error_ver103         T         [T] F, out-of-range HKF g abort
```

```
  aq_error_ver104        T        [T] F, abort on failed respeciation
  warning_ver637         T        [T] F
  error_ver109           T        [T] F
  do_not_reset_options   F        [F] T, prevents automatic resets
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     mcpv     cmpv     foHL     qHL
------------------------------------------------------------------------------
**warning ver099** no data for aqueous species, aq_output and aq_lagged_speciation disabled.

** Starting exploratory computational stage **
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
------------------------------------------------------------------------------
Exploratory stage generated:
Total number of compositions:       0
------------------------------------------------------------------------------
------------------------------------------------------------------------------
** Starting auto-refine computational stage **
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)
```

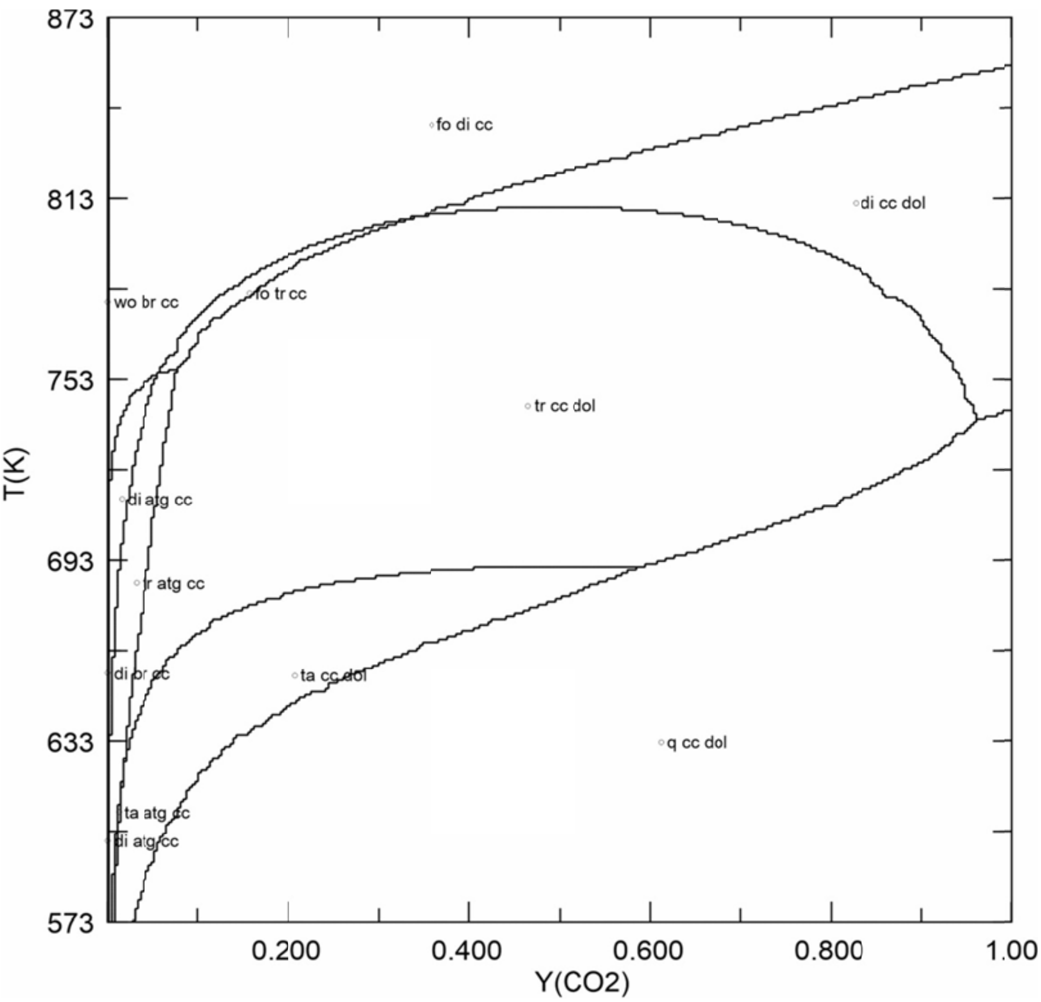
```
     refinement at level 4 involved   1893 minimizations
  5002 minimizations required of the theoretical limit of   98596
--------------------------------------------------------------------------------
    Timing                  min.        % of total
  Static G calculation       0.20833E-02       13.6
  Dynamic G calculation       0.0000           0.0
  Static LP              0.78125E-03       5.1
  Dynamic LP                 0.0000           0.0
  Successive QP              0.0000           0.0
  Total of above            0.28646E-02       18.6
  Total elapsed time        0.15365E-01       100.0
--------------------------------------------------------------------------------
End of job: ex5_2
```

(3) Plotting the calculated phase diagram (PSSECT)

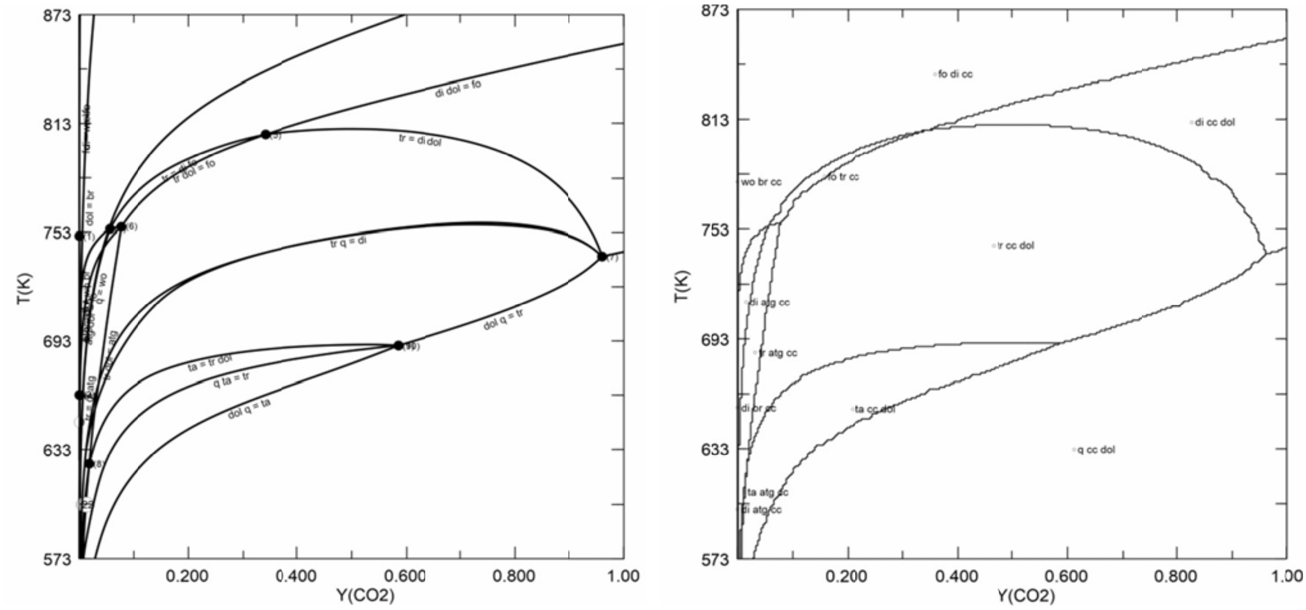
Run PSSECT to plot the calculated pseudosection:

```
C:\PERPLEX\Perplex7110>pssect

Perple_X release 7.1.10 Dec 21, 2024.
Copyright (C) 1986-2024 James A D Connolly <www.perplex.ethz.ch/copyright.html>.

Enter the project name (the name assigned in BUILD) [default = my_project]:
ex5_2

Reading Perple_X options from: perplex_option.dat

Perple_X plot options are currently set as:
    Keyword:               Value:     Permitted values [default]:
    axis_label_scale       1.20       [1.2] (rel)
    bounding_box :
                          0       [0] x-min (pts)
                          0       [0] y-min (pts)
                        800       [800] x-length (pts)
                        800       [800] y-length (pts)
    contour_t_interval       50.00    >0 [50.0]
    contour_p_interval     1000.00    >0 [1000.0]
    field_fill            T          [T] F
    field_label           T          [T] F
    numeric_field_label    F          [F] T, if T PSSECT writes list to *_assemblages.txt
    replicate_label        0.250      0->1 [0.025]
    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
   splines               T          [T] F
   tenth_ticks           F          [F] T
   text_scale            1.000      [1.] (rel)
   plot_extra_data       F          [T] F, to plot, e.g., experimental observations
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
There are   2 fields for: di atg cc
There are   2 fields for: tr cc dol
There are   3 fields for: fo tr cc
There are   2 fields for: di cc dol
There are   4 fields for: ta atg cc
```



Comparison between projection and pseudosection



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% (2Qz+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 Qz

(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\Perplex7110>convex

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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: hp62ver.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       [auto] manual off
    replicate_threshold     0.1E-1    [1e-2]; static opt; <0 => no replica test
    rep_dynamic_threshold   0.1E-2    [1d-3]; dynamic opt; <0 => no replica test
    re-refine               F         [F] T
    intermediate_savrpc     F         [F] T
    intermediate_savdyn     F         [F] T
    keep_all_rpcs           T         [T] F
  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 [     ], 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:
  P_stop (bar)            0.       [0]
  PT_freeze              F         [T] F
  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]
  approx_alpha           T         [T] F
  Anderson-Gruneisen      F         [F] T
  finite_strain_alpha     F         [F] T
  speciation_precision    0.1E-4    [1d-5] <1; absolute
  speciation_max_it       100       [100]
  function_tolerance_exp  0.8       [0.8] sets x in tol = epsmch^x
  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_lagged_speciation    F         [F] T
  aq_fractionation_simpl  F         [F] T
  aq_ion_H+              T         [T] F => use OH-
  aq_oxide_components     F         [F] T
  aq_solvent_solvus_tol   0.5       [0.5] 0-1
  aq_vapor_epsilon        1.0       [1.]
Input/Output options:
  timing                 T         [T] F
  auto_exclude           T         [T] F
  output_iteration_detai  F         [F] T
  output_iteration_g      F         [F] T
Error/warning control options:
  pause_on_error          T         [T] F
  max_warn_limit           5        [5]
  warn_interactive        T         [T] F
  aq_error_ver100         F         [F] T, abort during iteration
  aq_error_ver101         T         [T] F, solute undersaturation abort
  aq_error_ver102         T         [T] F, pure + impure solvent abort
  aq_error_ver103         T         [T] F, out-of-range HKF g abort
```

```
  aq_error_ver104        T        [T] F, abort on failed respeciation
  warning_ver637         T        [T] F
  error_ver109           T        [T] F
  do_not_reset_options   F        [F] T, prevents automatic resets
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     mcpv     cmpv     foHL     qHL
------------------------------------------------------------------------------
------------------------------------------------------------------------------
Summary of saturated-component entities:
 for: SiO2
  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
finished with equilibrium (     2) ta dol = tr
finished with equilibrium (     3) dol = ta cc
finished with equilibrium (     4) dol = tr cc
finished with equilibrium (     5) mag = ta
finished with equilibrium (     5) mag = ta
finished with equilibrium (     6) dol mag = tr
**warning ver020** sfol2
finished with equilibrium (     7) tr cc = di

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

finished with equilibrium (     8) dol = di
finished with equilibrium (     8) dol = di
finished with equilibrium (     8) dol = di
finished with equilibrium (     9) ta = en
finished with equilibrium (    10) mag = en
finished with equilibrium (    11) dol en = tr
finished with equilibrium (    10) mag = en
finished with equilibrium (    10) mag = en
finished with equilibrium (    11) dol en = tr
finished with equilibrium (    12) tr = di en
finished with equilibrium (     8) dol = di
finished with equilibrium (    13) ta = anth
finished with equilibrium (    14) anth = en
Testing divariant assemblage      2,      2 assemblages remaining to be tested.
```

```
finished with equilibrium (     7) tr cc = di
Testing divariant assemblage     3,     2 assemblages remaining to be tested.
finished with equilibrium (    15) cc = wo
Testing divariant assemblage     4,     2 assemblages remaining to be tested.
Testing divariant assemblage     5,     3 assemblages remaining to be tested.
Testing divariant assemblage     6,     3 assemblages remaining to be tested.
Testing divariant assemblage     7,     2 assemblages remaining to be tested.
Testing divariant assemblage     8,     2 assemblages remaining to be tested.
Testing divariant assemblage     9,     2 assemblages remaining to be tested.
Testing divariant assemblage    10,     3 assemblages remaining to be tested.
Testing divariant assemblage    11,     3 assemblages remaining to be tested.
Testing divariant assemblage    12,     3 assemblages remaining to be tested.
Testing divariant assemblage    13,     3 assemblages remaining to be tested.
Testing divariant assemblage    14,     3 assemblages remaining to be tested.
Testing divariant assemblage    15,     2 assemblages remaining to be tested.
Testing divariant assemblage    16,     2 assemblages remaining to be tested.
Testing divariant assemblage    17,     1 assemblages remaining to be tested.
Testing divariant assemblage    18,     0 assemblages remaining to be tested.
Testing divariant assemblage    19,     1 assemblages remaining to be tested.
Testing divariant assemblage    20,     0 assemblages remaining to be tested.
Testing divariant assemblage    21,     0 assemblages remaining to be tested.
Testing divariant assemblage    22,     0 assemblages remaining to be tested.
```

(3) Plotting the calculated phase diagram (PSVDRAW)

Run PSVDRAW to plot the calculated phase diagram:

```
C:\PERPLEX\Perplex7110>psvdraw

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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)
   contour_t_interval       50.00    >0 [50.0]
   contour_p_interval     1000.00    >0 [1000.0]
   field_fill           T         [T] F
   field_label           T         [T] F
   numeric_field_label    F         [F] T, if T PSSECT writes list to *_assemblages.txt
   replicate_label        0.250     0->1 [0.025]
   field_label_scale      0.75      [0.72] (rel)
   font                  Helvetica
```
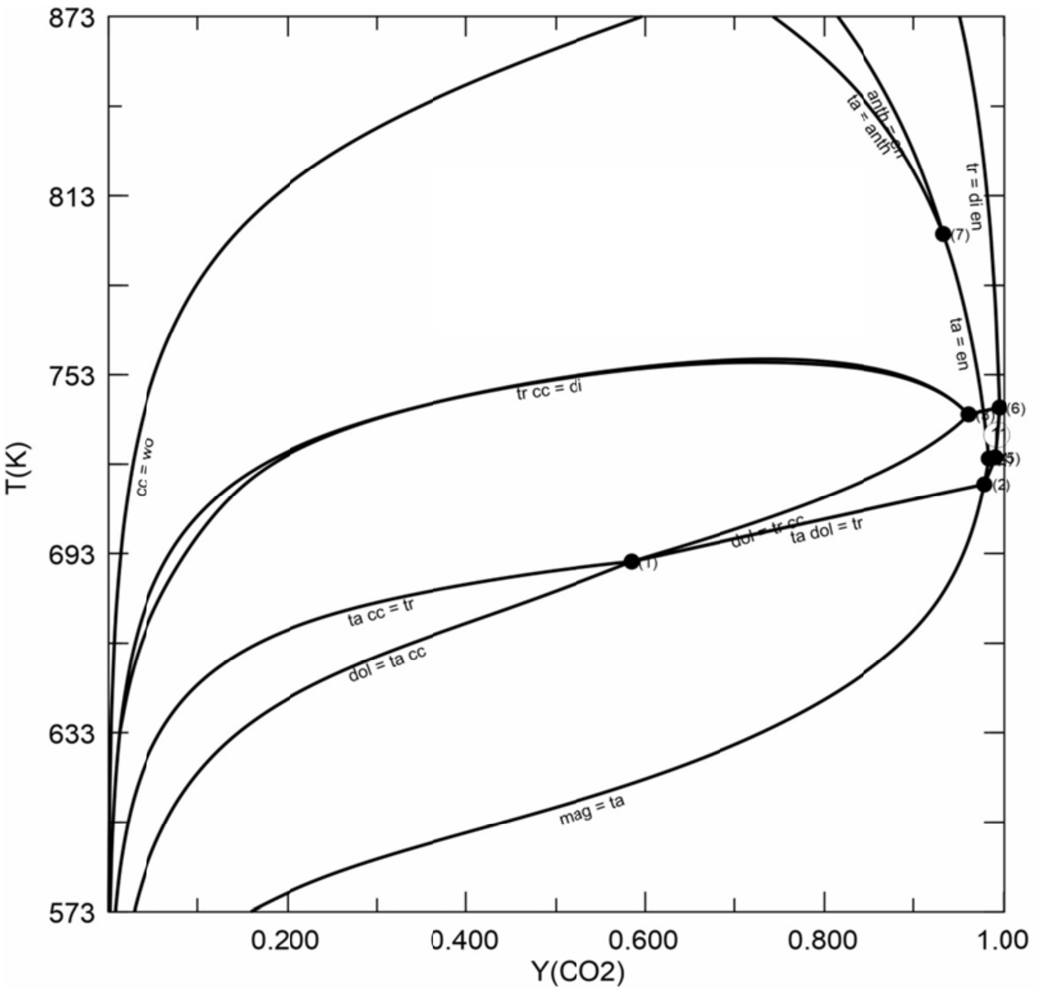

```
grid                F         [F] T
half_ticks          T         [T] F
line_width          1.00      0-99 [1.] (pts)
picture_transformation :
                    0.180     [0.18] x-scale (rel)
                    0.180     [0.18] y-scale (rel)
                    130.      [0.18] x-translation (pts)
                    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
splines             T         [T] F
tenth_ticks         F         [F] T
text_scale          1.000     [1.] (rel)
plot_extra_data     F         [T] F, to plot, e.g., experimental observations


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_3.ps

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



Ex. 5.4 – Isobaric T-XCO_2 pseudosection of a siliceous limestone for the composition 6Qz–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 6Qz + 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\Perplex7110>vertex

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Enter the project name (the name assigned in BUILD) [default = my_project]:
ex5_4

Reading problem definition from file: ex5_4.dat
Reading thermodynamic data from file: hp62ver.dat
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       [auto] manual off
    replicate_threshold     0.1E-1    [1e-2]; static opt; <0 => no replica test
    rep_dynamic_threshold   0.1E-2    [1d-3]; dynamic opt; <0 => no replica test
    re-refine              F         [F] T
    intermediate_savrpc     F         [F] T
    intermediate_savdyn     F         [F] T
    keep_all_rpcs          T         [T] F
```

```
Free energy minimization options:
  MINFRC_diff_increment   0.1E-6    [1e-7] 1e-3 => 1e-9
  MINFXC_solver           0        [0] >= 0 - speci2, -1 - MINFXC
  optimization_max_it     40       [40] >1
  optimization_precision  0.1E-3    [1e-4], 1e-1 => 1e-6, absolute
  dynamic_LP_start        war      [warm] cold hot
  static_LP_start         war      [hot] cold warm
  order_check             F        [F] T
  refinement_points       5        [auto] 1->14
  scatter-points          T        [T] F
  scatter-increment       0.1E-1    [1e-2] 1e-2 => 1e-7
  solvus_tolerance_II     aut      [0.2] 0->1
  zero_mode               0.1E-5    [1e-6] 0->1; < 0 => off
2D grid options:
  x_nodes                20 / 40   [20/40] >0, <2048; effective x-resolution   20 / 313 nodes
  y_nodes                20 / 40   [20/40] >0, <2048; effective y-resolution   20 / 313 nodes
  grid_levels            1 / 4     [1/4] >0, <10
  linear_model           on        [on] off
Solution subdivision options:
  initial_resolution:     0.2000    [1/5] 0->1; 0 => off
  stretch_factor          0.0020    [2d-3] >0
  non_linear_switch       F        [F] T
  subdivision_override    off      [lin] off str
  refine_endmembers       F        [F] T
Thermodynamic options:
  P_stop (bar)            0.       [0]
  PT_freeze               F        [T] F
  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]
  approx_alpha            T        [T] F
  Anderson-Gruneisen      F        [F] T
  finite_strain_alpha     F        [F] T
  speciation_precision    0.1E-4    [1d-5] <1; absolute
  speciation_max_it       100      [100]
  function_tolerance_exp  0.8      [0.8] sets x in tol = epsmch^x
  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_lagged_speciation    F        [F] T
  aq_fractionation_simpl  F        [F] T
  aq_ion_H+               T        [T] F => use OH-
  aq_oxide_components     F        [F] T
  aq_solvent_solvus_tol   0.5      [0.5] 0-1
  aq_vapor_epsilon        1.0      [1.]
Input/Output options:
  timing                  T        [T] F
  auto_exclude            T        [T] F
  output_iteration_detai  F        [F] T
  output_iteration_g      F        [F] T
  logarithmic_p           F        [F] T
```

```
    logarithmic_X          F        [F] T
    bad_number             NaN      [NaN]
    interim_results        aut      [auto] off manual
  Information file output options:
    option_list_files      F        [F] T; echo computational options
    pseudocompound_file    F        [F] T; echo static pseudocompound compositions
    auto_refine_file       F        [T] F; echo auto-refine compositions
    seismic_data_file      T        [F] T; echo seismic wavespeed options
  Error/warning control options:
    pause_on_error         T        [T] F
    max_warn_limit           5      [5]
    warn_interactive       T        [T] F
    aq_error_ver100        F        [F] T, abort during iteration
    aq_error_ver101        T        [T] F, solute undersaturation abort
    aq_error_ver102        T        [T] F, pure + impure solvent abort
    aq_error_ver103        T        [T] F, out-of-range HKF g abort
    aq_error_ver104        T        [T] F, abort on failed respeciation
    warning_ver637         T        [T] F
    error_ver109           T        [T] F
    do_not_reset_options   F        [F] T, prevents automatic resets
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     mcpv     cmpv     foHL     qHL
--------------------------------------------------------------------------------
**warning ver099** no data for aqueous species, aq_output and aq_lagged_speciation disabled.

** Starting exploratory computational stage **
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
--------------------------------------------------------------------------------
Exploratory stage generated:
Total number of compositions:       0
--------------------------------------------------------------------------------
--------------------------------------------------------------------------------
** Starting auto-refine computational stage **
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
-------------------------------------------------------------------------------
    Timing                  min.        % of total
 Static G calculation      0.15625E-02       12.2
 Dynamic G calculation      0.0000           0.0
 Static LP                0.52083E-03       4.1
 Dynamic LP                 0.0000           0.0
 Successive QP              0.0000           0.0
 Total of above            0.20833E-02       16.3
 Total elapsed time        0.12760E-01      100.0
-------------------------------------------------------------------------------
End of job: ex5_4
```

(3) Plotting the calculated phase diagram (PSSECT)

Run PSSECT to plot the calculated pseudosection:

```
C:\PERPLEX\Perplex7110>pssect

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Enter the project name (the name assigned in BUILD) [default = my_project]:
ex5_4

Reading Perple_X options from: perplex_option.dat

Perple_X plot options are currently set as:
   Keyword:              Value:     Permitted values [default]:
   axis_label_scale       1.20       [1.2] (rel)
   bounding_box :
                              0      [0] x-min (pts)
                              0      [0] y-min (pts)
                            800      [800] x-length (pts)
                            800      [800] y-length (pts)
   contour_t_interval       50.00     >0 [50.0]
   contour_p_interval     1000.00     >0 [1000.0]
```
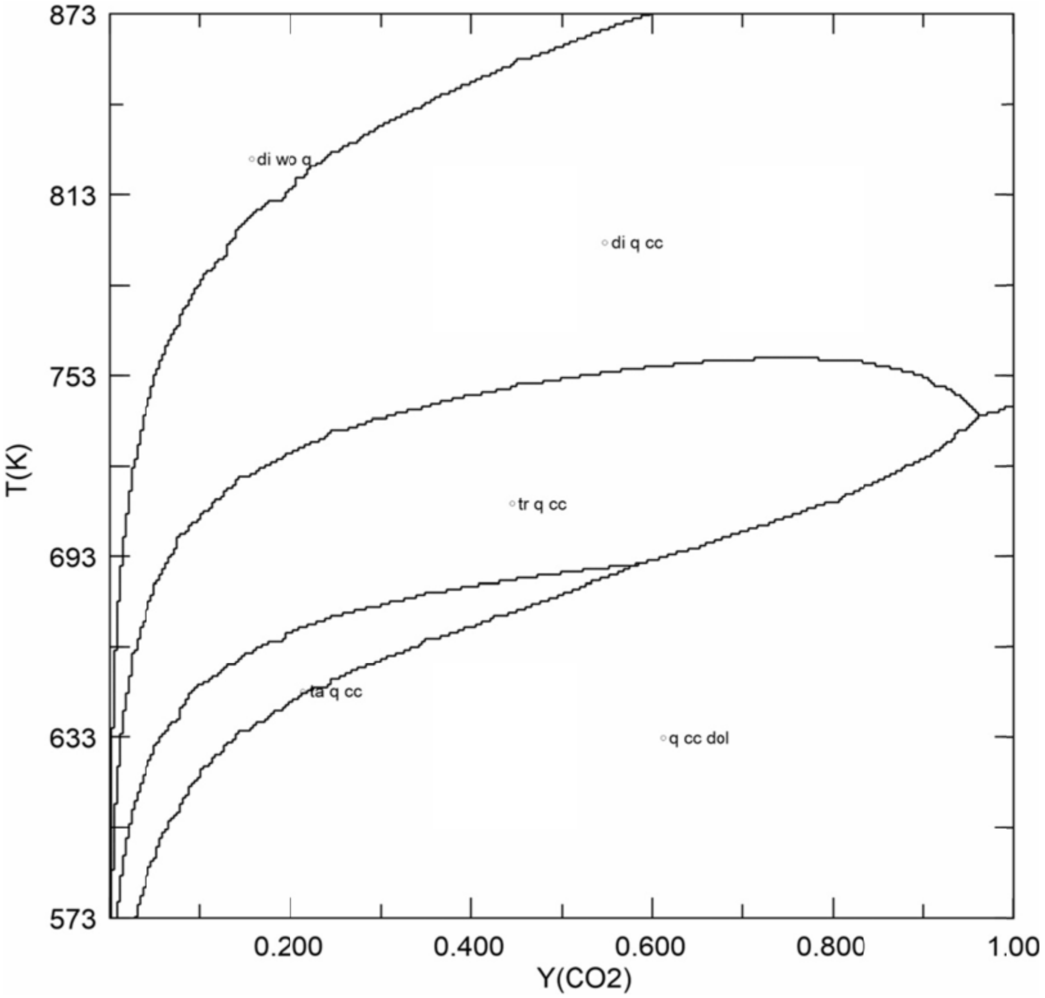
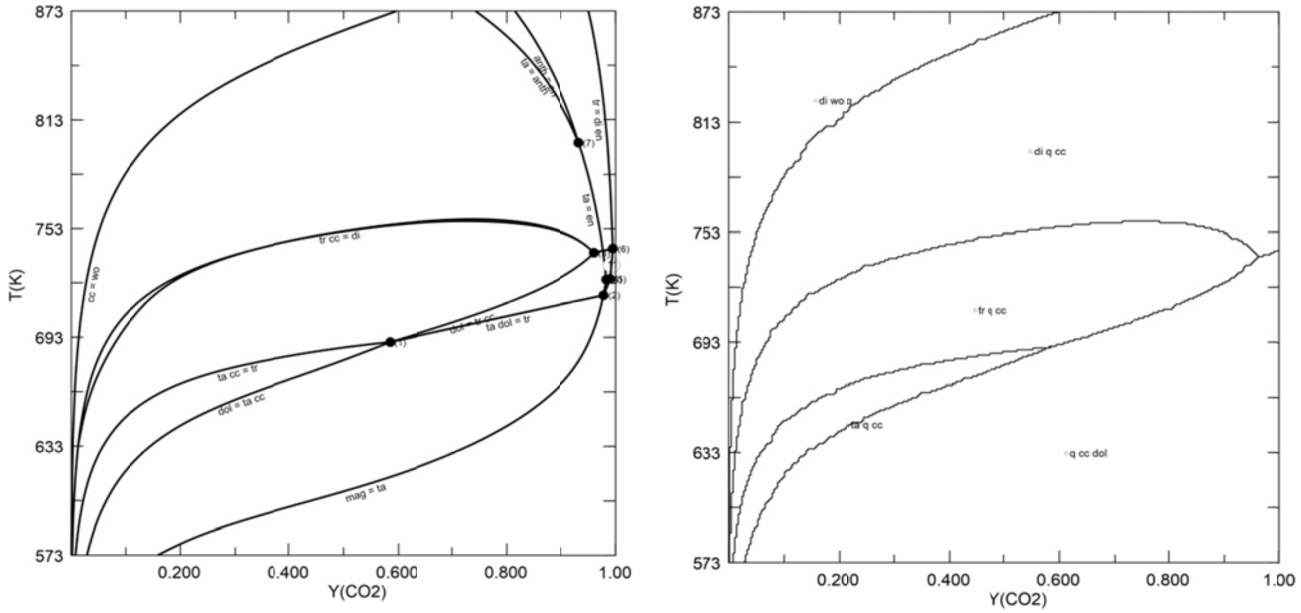

```
   field_fill           T         [T] F
   field_label          T         [T] F
   numeric_field_label    F         [F] T, if T PSSECT writes list to *_assemblages.txt
   replicate_label       0.250     0->1 [0.025]
   field_label_scale      0.75      [0.72] (rel)
   font                  Helvetica
   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
   splines              T         [T] F
   tenth_ticks          F         [F] T
   text_scale           1.000     [1.] (rel)
   plot_extra_data       F         [T] F, to plot, e.g., experimental observations
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
There are   2 fields for: ta q cc
```



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-Mgs *solvi* is investigated by calculating the same phase diagram at different pressures.

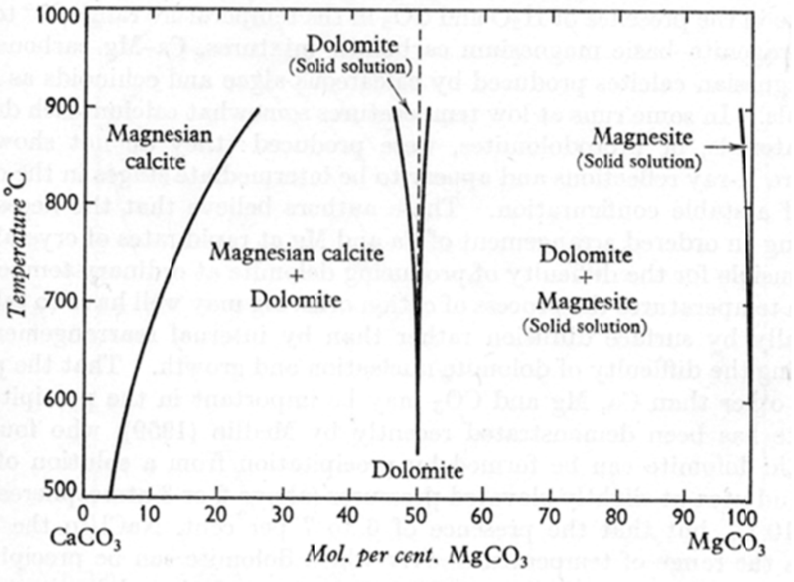


Fig. 53. The $CaCO_3$–$MgCO_3$ system, at CO_2 pressures sufficient to prevent decomposition of the carbonates (after Goldsmith, 1959).

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\Perplex7110>build

Perple_X release 7.1.10 Dec 21, 2024.
Copyright (C) 1986-2024 James A D Connolly <www.perplex.ethz.ch/copyright.html>.
```

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

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

The problem definition file will be named: ex6_5kbar.dat

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

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
6 - 0-d Infiltration-reaction-fractionation
7 - 2-d Phase fractionation (FRAC2D and TITRATE reactive transport models)
8 - (pseudo-)Ternary liquidus/solidus surfaces
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

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*
  14 - X(CO2) H2O-CO2 Pitzer & Sterner 94; Holland & Powell mixing 03
  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
  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  - MRK DeSantis et al 1974
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          20      20        20 x  20 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
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 read the commentary in solution_model.dat
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\Perplex7110>vertex

Perple_X release 7.1.10 Dec 21, 2024.
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Enter the project name (the name assigned in BUILD) [default = my_project]:
ex6_5kbar
```

```
Reading problem definition from file: ex6_5kbar.dat
Reading thermodynamic data from file: hp62ver.dat
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: not requested
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        [auto] manual off
    replicate_threshold    0.1E-1     [1e-2]; static opt; <0 => no replica test
    rep_dynamic_threshold  0.1E-2     [1d-3]; dynamic opt; <0 => no replica test
    re-refine              F          [F] T
    intermediate_savrpc    F          [F] T
    intermediate_savdyn    F          [F] T
    keep_all_rpcs          T          [T] F
  Free energy minimization options:
    MINFRC_diff_increment  0.1E-6     [1e-7] 1e-3 => 1e-9
    MINFXC_solver          0          [0] >= 0 - speci2, -1 - MINFXC
    optimization_max_it    40         [40] >1
    optimization_precision 0.1E-3     [1e-4], 1e-1 => 1e-6, absolute
    dynamic_LP_start       war        [warm] cold hot
    static_LP_start        war        [hot] cold warm
    order_check            F          [F] T
    refinement_points      4          [auto] 1->14
    scatter-points         T          [T] F
    scatter-increment      0.1E-1     [1e-2] 1e-2 => 1e-7
    solvus_tolerance_II    aut        [0.2] 0->1
    zero_mode              0.1E-5     [1e-6] 0->1; < 0 => off
  2D grid options:
    x_nodes                20 / 40    [20/40] >0, <2048; effective x-resolution   20 / 313 nodes
    y_nodes                20 / 40    [20/40] >0, <2048; effective y-resolution   20 / 313 nodes
    grid_levels            1 / 4      [1/4] >0, <10
    linear_model           on         [on] off
  Composition options:
    closed_c_space         T          [T] F
  Solution subdivision options:
    initial_resolution:    0.2000     [1/5] 0->1; 0 => off
    stretch_factor         0.0020     [2d-3] >0
    non_linear_switch      F          [F] T
    subdivision_override   off        [lin] off str
    refine_endmembers      F          [F] T
  Thermodynamic options:
    P_stop (bar)           0.         [0]
```

```
  PT_freeze              F        [T] F
  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]
  approx_alpha           T        [T] F
  Anderson-Gruneisen     F        [F] T
  finite_strain_alpha    F        [F] T
  speciation_precision   0.1E-4   [1d-5] <1; absolute
  speciation_max_it      100      [100]
  function_tolerance_exp 0.8      [0.8] sets x in tol = epsmch^x
  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_lagged_speciation   F        [F] T
  aq_fractionation_simpl F        [F] T
  aq_ion_H+              T        [T] F => use OH-
  aq_oxide_components    F        [F] T
  aq_solvent_solvus_tol  0.5      [0.5] 0-1
  aq_vapor_epsilon       1.0      [1.]
 Input/Output options:
  timing                 T        [T] F
  auto_exclude           T        [T] F
  output_iteration_detai F        [F] T
  output_iteration_g     F        [F] T
  logarithmic_p          F        [F] T
  logarithmic_X          F        [F] T
  bad_number             NaN      [NaN]
  interim_results        aut      [auto] off manual
 Information file output options:
  option_list_files      F        [F] T; echo computational options
  pseudocompound_file    T        [F] T; echo static pseudocompound compositions
  auto_refine_file       F        [T] F; echo auto-refine compositions
  seismic_data_file      T        [F] T; echo seismic wavespeed options
 Error/warning control options:
  pause_on_error         T        [T] F
  max_warn_limit         5        [5]
  warn_interactive       T        [T] F
  aq_error_ver100        F        [F] T, abort during iteration
  aq_error_ver101        T        [T] F, solute undersaturation abort
  aq_error_ver102        T        [T] F, pure + impure solvent abort
  aq_error_ver103        T        [T] F, out-of-range HKF g abort
  aq_error_ver104        T        [T] F, abort on failed respeciation
  warning_ver637         T        [T] F
  error_ver109           T        [T] F
  do_not_reset_options   F        [F] T, prevents automatic resets
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
     4 pseudocompounds generated for: Do(AE)
**warning ver114** the following endmembers are missing for Cc(AE):
 sid
     4 pseudocompounds generated for: Cc(AE)
Total number of pseudocompounds:      8

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 **
100.0% done with low level grid.
--------------------------------------------------------------------------------
Exploratory stage generated:
     14 compositions for: Do(AE)
     35 compositions for: Cc(AE)
Total number of compositions:      49
--------------------------------------------------------------------------------
--------------------------------------------------------------------------------
```

This is the beginning of the AUTO-REFINE STAGE

```
** Starting auto-refine computational stage **
100.0% done with low level grid.

Beginning grid refinement stage.

   164 grid cells to be refined at grid level 2
      refinement at level 2 involved     347 minimizations
  1947 minimizations required of the theoretical limit of     6241
   316 grid cells to be refined at grid level 3
      ...working (    154 minimizations done)
      refinement at level 3 involved     621 minimizations
  2568 minimizations required of the theoretical limit of    24649
   620 grid cells to be refined at grid level 4
      ...working (     34 minimizations done)
      ...working (    535 minimizations done)
      ...working (  1036 minimizations done)
```

```
     refinement at level 4 involved   1210 minimizations
  3778 minimizations required of the theoretical limit of   98596
--------------------------------------------------------------------------------
    Timing                   min.        % of total
  Static G calculation       0.0000           0.0
  Dynamic G calculation      0.33854E-02       13.5
  Static LP               0.26042E-03       1.0
  Dynamic LP               0.26042E-02       10.4
  Successive QP            0.62500E-02       25.0
  Total of above           0.12500E-01       50.0
  Total elapsed time       0.25000E-01       100.0
--------------------------------------------------------------------------------
End of job: ex6_5kbar
```

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\Perplex7110>pssect

Perple_X release 7.1.10 Dec 21, 2024.
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Enter the project name (the name assigned in BUILD) [default = my_project]:
ex6_5kbar

Reading Perple_X options from: perplex_option.dat

--------------------------------------------------------------------------------
Perple_X plot options are currently set as:

    Keyword:              Value:     Permitted values [default]:
    axis_label_scale       1.20       [1.2] (rel)
    bounding_box :
                            0      [0] x-min (pts)
                            0      [0] y-min (pts)
                          800      [800] x-length (pts)
                          800      [800] y-length (pts)
    contour_t_interval       50.00     >0 [50.0]
    contour_p_interval     1000.00     >0 [1000.0]
    field_fill            T         [T] F
    field_label            T         [T] F
    numeric_field_label    F         [F] T, if T PSSECT writes list to *_assemblages.txt
    replicate_label        0.250      0->1 [0.025]
    field_label_scale      0.75       [0.72] (rel)
    font                   Helvetica
    grid                   F         [F] T
```
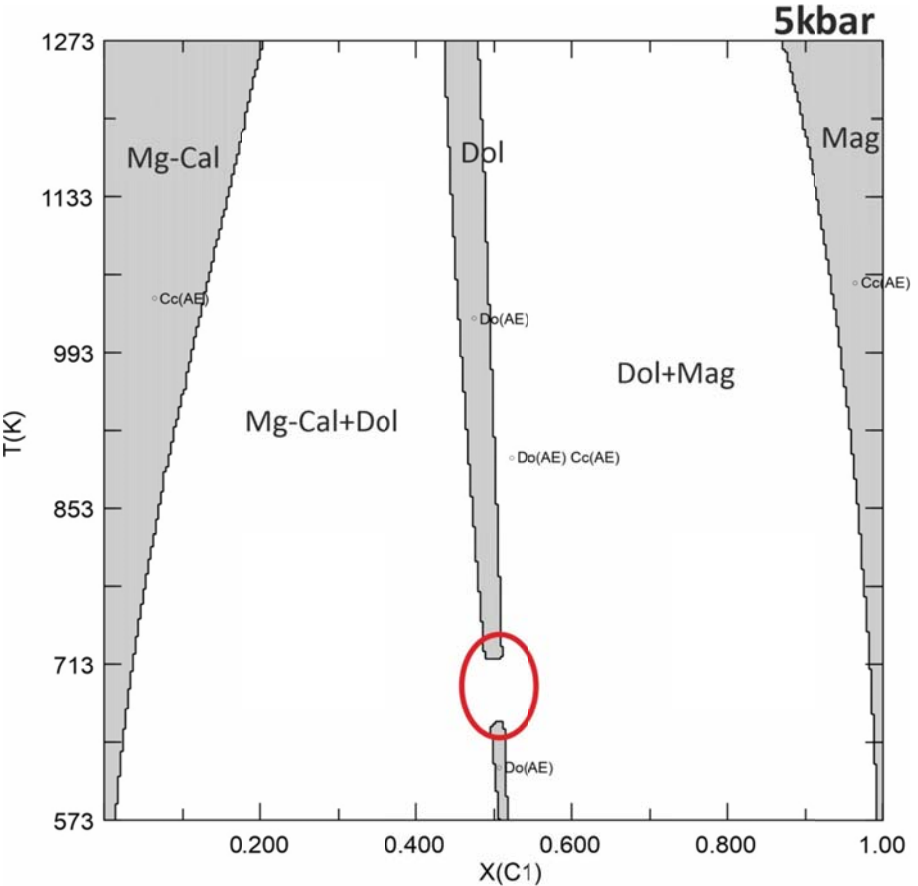

```
   half_ticks            T          [T] F
   line_width            1.00       0-99 [1.] (pts)
   picture_transformation :
                         0.180      [0.18] x-scale (rel)
                         0.180      [0.18] y-scale (rel)
                          130.      [0.18] x-translation (pts)
                          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
   splines               T          [T] F
   tenth_ticks           F          [F] T
   text_scale            1.000      [1.] (rel)
   plot_extra_data       F          [T] F, to plot, e.g., experimental observations
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)
There are   2 fields for: Do(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

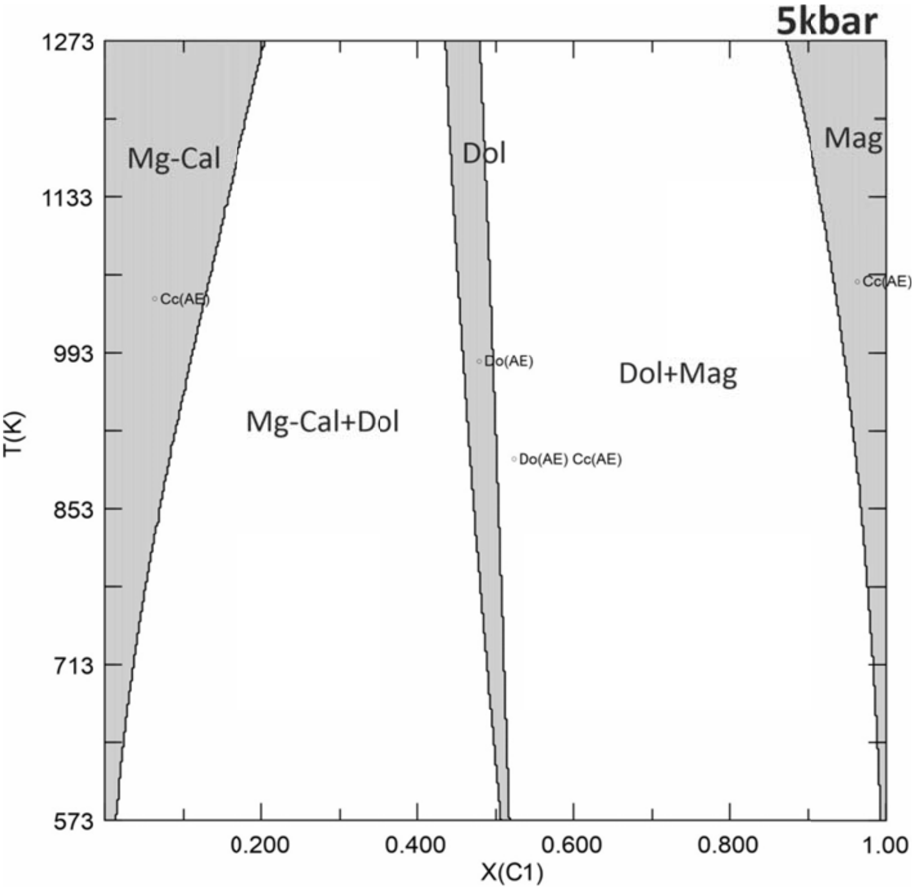
For gridded minimization, VERTEX uses a multilevel grid refinement strategy in which phase relations are mapped on an initial grid of resolution x_nodes * y_nodes. This grid is refined a number of times equal to (grid_levels – 1) by bisection (Connolly 2005). The **x_nodes, y_nodes, grid_levels** parameters 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 20 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	10 60 | [10 40] exploratory and auto-refine (grid parameters keyword group), lowest-level x grid resolution
y_nodes	10 60 | [10 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.

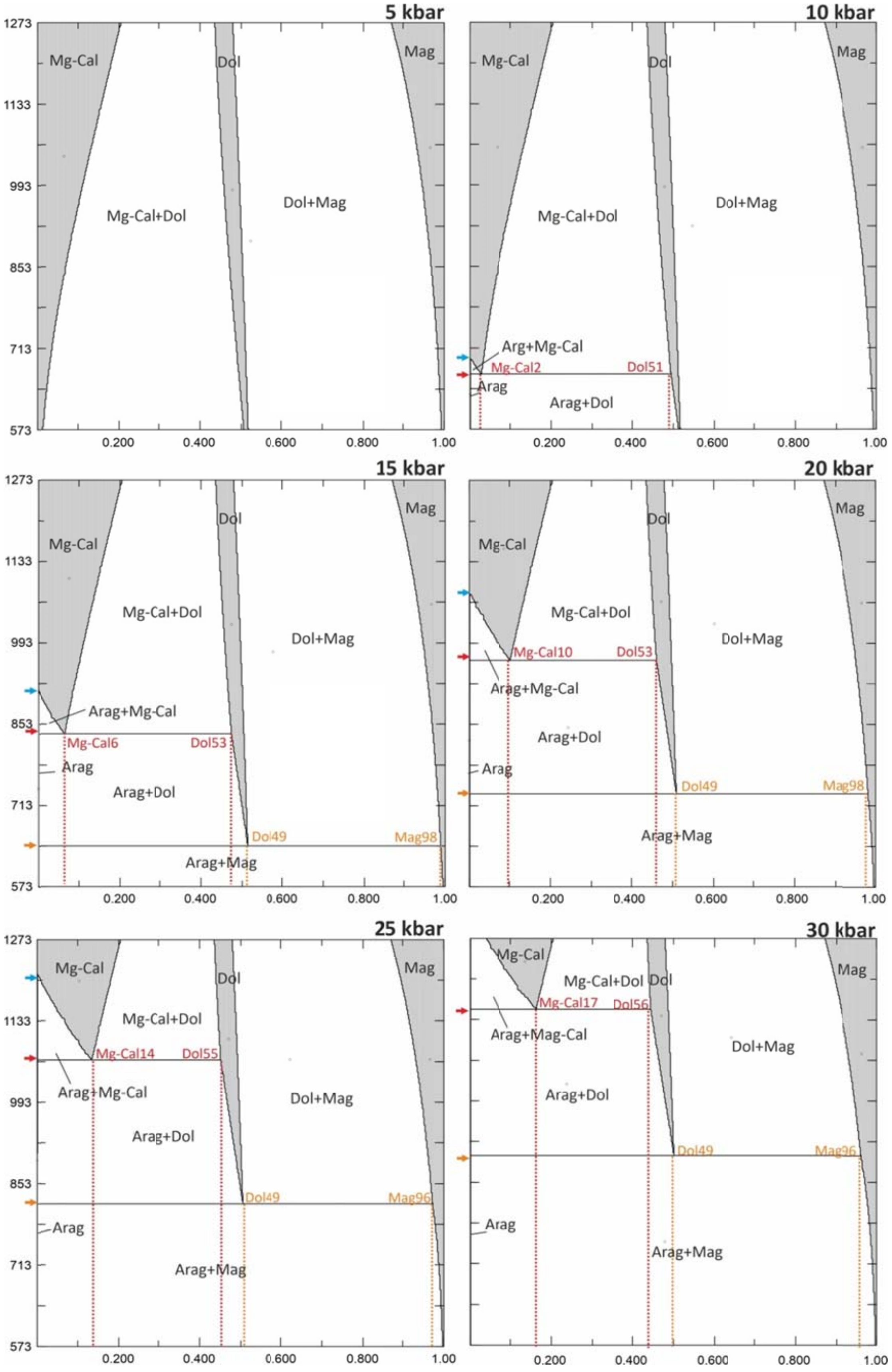


(5) Exploring the influence of pressure on the Cal-Dol and Dol-Mag *solvi*

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\Perplex7110>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]:
ex7

The problem definition file will be named: ex7.dat

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

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
    6 - 0-d Infiltration-reaction-fractionation
    7 - 2-d Phase fractionation (FRAC2D and TITRATE reactive transport models)
    8 - (pseudo-)Ternary liquidus/solidus surfaces
```

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.

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

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*
14 - X(CO2) H2O-CO2 Pitzer & Sterner 94; Holland & Powell mixing 03
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
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 - MRK DeSantis et al 1974

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 read the commentary in solution_model.dat
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\Perplex7110>convex

Perple_X release 7.1.10 Dec 21, 2024.
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Enter the project name (the name assigned in BUILD) [default = my_project]:
ex7

Reading problem definition from file: ex7.dat
Reading thermodynamic data from file: hp62ver.dat
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: ex7_pseudocompound_glossary.txt
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       [auto] manual off
   replicate_threshold     0.1E-1    [1e-2]; static opt; <0 => no replica test
   rep_dynamic_threshold   0.1E-2    [1d-3]; dynamic opt; <0 => no replica test
   re-refine               F         [F] T
   intermediate_savrpc     F         [F] T
   intermediate_savdyn     F         [F] T
   keep_all_rpcs           T         [T] F
  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 [     ], 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:
  P_stop (bar)           0.       [0]
  PT_freeze              F         [T] F
  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]
  approx_alpha           T         [T] F
  Anderson-Gruneisen      F         [F] T
  finite_strain_alpha     F         [F] T
  speciation_precision    0.1E-4    [1d-5] <1; absolute
  speciation_max_it       100       [100]
  function_tolerance_exp  0.8       [0.8] sets x in tol = epsmch^x
  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_lagged_speciation    F         [F] T
  aq_fractionation_simpl  F         [F] T
  aq_ion_H+              T         [T] F => use OH-
  aq_oxide_components     F         [F] T
  aq_solvent_solvus_tol   0.5       [0.5] 0-1
  aq_vapor_epsilon       1.0       [1.]
Input/Output options:
  timing                T         [T] F
  auto_exclude           T         [T] F
  output_iteration_detai  F         [F] T
  output_iteration_g      F         [F] T
Error/warning control options:
  pause_on_error         T         [T] F
  max_warn_limit          5        [5]
  warn_interactive       T         [T] F
  aq_error_ver100        F         [F] T, abort during iteration
  aq_error_ver101        T         [T] F, solute undersaturation abort
  aq_error_ver102        T         [T] F, pure + impure solvent abort
  aq_error_ver103        T         [T] F, out-of-range HKF g abort
```

```
    aq_error_ver104        T        [T] F, abort on failed respeciation
    warning_ver637         T        [T] F
    error_ver109           T        [T] F
    do_not_reset_options    F        [F] T, prevents automatic resets
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
     16 pseudocompounds generated for: Do(AE)
**warning ver114** the following endmembers are missing for Cc(AE):
  sid
     16 pseudocompounds generated for: Cc(AE)
Total number of pseudocompounds:      32

Summary of included solution models:
Do(AE)     Cc(AE)
--------------------------------------------------------------------------------
** Starting exploratory 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.
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,      5 assemblages remaining to be tested.
Testing divariant assemblage      6,      6 assemblages remaining to be tested.
Testing divariant assemblage      7,      6 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      8,      6 assemblages remaining to be tested.
Testing divariant assemblage      9,      7 assemblages remaining to be tested.
**warning ver066** Metastable assemblage into FLIPIT:
    ma_98.50 arag
v = 30000.0      573.000      1.00000      0.00000      0.00000
Testing divariant assemblage     10,      8 assemblages remaining to be tested.
Testing divariant assemblage     11,      7 assemblages remaining to be tested.
Testing divariant assemblage     12,      7 assemblages remaining to be tested.
Testing divariant assemblage     13,      7 assemblages remaining to be tested.
Testing divariant assemblage     14,      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     15,      5 assemblages remaining to be tested.
Testing divariant assemblage     16,      4 assemblages remaining to be tested.
Testing divariant assemblage     17,      5 assemblages remaining to be tested.
Testing divariant assemblage     18,      5 assemblages remaining to be tested.
Testing divariant assemblage     19,      4 assemblages remaining to be tested.
```

```
**warning ver066** Metastable assemblage into FLIPIT:
    mag_86.2 cc_55.1
v = 5000.00      1203.00      1.00000      0.00000      0.00000
Testing divariant assemblage     20,      3 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,      4 assemblages remaining to be tested.
Testing divariant assemblage     24,      3 assemblages remaining to be tested.
Testing divariant assemblage     25,      2 assemblages remaining to be tested.
Testing divariant assemblage     26,      2 assemblages remaining to be tested.
Testing divariant assemblage     27,      2 assemblages remaining to be tested.
Testing divariant assemblage     28,      1 assemblages remaining to be tested.
**warning ver066** Metastable assemblage into FLIPIT:
    arag     mag_18.5
v = 30000.0      1133.00      1.00000      0.00000      0.00000
Testing divariant assemblage     29,      0 assemblages remaining to be tested.

Compositions for simplicial model: Do(AE)
               Minimum        Maximum
    cc          0.49000        0.55125
    mag          0.44875        0.51000

Compositions for simplicial model: Cc(AE)
               Minimum        Maximum
    mag          0.61562E-01    0.98500
    cc          0.15000E-01    0.93844
--------------------------------------------------------------------------------
Solution model summary:
     10 pseudocompounds generated for: Do(AE)
     48 pseudocompounds generated for: Cc(AE)
Total number of pseudocompounds:      58

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) arag = Cc(AE)(ma_98.50)
Testing divariant assemblage      2,      3 assemblages remaining to be tested.
finished with equilibrium (     2) Cc(AE)(ma_98.50) Do(AE)(cc_49.0) = Cc(AE)(mag_96.4)
finished with equilibrium (     3) Cc(AE)(ma_98.50) arag = Do(AE)(cc_49.0)
finished with equilibrium (     4) Cc(AE)(ma_98.50) arag = Cc(AE)(mag_96.4)
finished with equilibrium (     5) Cc(AE)(mag_96.4) arag = Do(AE)(cc_49.0)
Testing divariant assemblage      3,      4 assemblages remaining to be tested.
finished with equilibrium (     6) Do(AE)(cc_49.0) Cc(AE)(mag_2.1) = Do(AE)(cc_51.0)
finished with equilibrium (     7) Do(AE)(cc_49.0) arag = Cc(AE)(mag_2.1)
```

```
finished with equilibrium (    8) Do(AE)(cc_49.0) arag = Do(AE)(cc_51.0)
finished with equilibrium (    9) Do(AE)(cc_51.0) arag = Cc(AE)(mag_2.1)
finished with equilibrium (   10) Cc(AE)(mag_2.1) Do(AE)(cc_51.0) = Cc(AE)(mag_4.1)
finished with equilibrium (   11) arag Cc(AE)(mag_4.1) = Cc(AE)(mag_2.1)
finished with equilibrium (   12) Do(AE)(cc_51.0) arag = Cc(AE)(mag_4.1)
finished with equilibrium (   13) Do(AE)(cc_51.0) arag = Cc(AE)(mag_6.2)
finished with equilibrium (   14) Do(AE)(cc_51.0) Cc(AE)(mag_4.1) = Cc(AE)(mag_6.2)
finished with equilibrium (   15) arag Cc(AE)(mag_6.2) = Cc(AE)(mag_4.1)
finished with equilibrium (   16) Do(AE)(cc_51.0) arag = Do(AE)(cc_53.1)
finished with equilibrium (   17) Do(AE)(cc_51.0) Cc(AE)(mag_6.2) = Do(AE)(cc_53.1)
finished with equilibrium (   18) arag Do(AE)(cc_53.1) = Cc(AE)(mag_6.2)
finished with equilibrium (   19) arag Cc(AE)(mag_8.2) = Cc(AE)(mag_6.2)
finished with equilibrium (   20) arag Do(AE)(cc_53.1) = Cc(AE)(mag_8.2)
finished with equilibrium (   21) Cc(AE)(mag_6.2) Do(AE)(cc_53.1) = Cc(AE)(mag_8.2)
finished with equilibrium (   22) arag Do(AE)(cc_53.1) = Cc(AE)(mag_10.3)
finished with equilibrium (   23) arag Cc(AE)(mag_10.3) = Cc(AE)(mag_8.2)
finished with equilibrium (   24) Do(AE)(cc_53.1) Cc(AE)(mag_8.2) = Cc(AE)(mag_10.3)
finished with equilibrium (   25) arag Do(AE)(cc_53.1) = Do(AE)(cc_55.1)
finished with equilibrium (   26) arag Do(AE)(cc_55.1) = Cc(AE)(mag_10.3)
finished with equilibrium (   27) Do(AE)(cc_53.1) Cc(AE)(mag_10.3) = Do(AE)(cc_55.1)
finished with equilibrium (   28) arag Cc(AE)(mag_12.3) = Cc(AE)(mag_10.3)
finished with equilibrium (   29) arag Do(AE)(cc_55.1) = Cc(AE)(mag_12.3)
finished with equilibrium (   30) Cc(AE)(mag_10.3) Do(AE)(cc_55.1) = Cc(AE)(mag_12.3)
finished with equilibrium (   31) arag Do(AE)(cc_55.1) = Cc(AE)(mag_14.4)
finished with equilibrium (   32) arag Cc(AE)(mag_14.4) = Cc(AE)(mag_12.3)
finished with equilibrium (   33) Do(AE)(cc_55.1) Cc(AE)(mag_12.3) = Cc(AE)(mag_14.4)
finished with equilibrium (   34) arag Do(AE)(cc_55.1) = Cc(AE)(mag_16.4)
finished with equilibrium (   35) arag Cc(AE)(mag_16.4) = Cc(AE)(mag_14.4)
finished with equilibrium (   36) Do(AE)(cc_55.1) Cc(AE)(mag_14.4) = Cc(AE)(mag_16.4)
Testing divariant assemblage      4,      5 assemblages remaining to be tested.
finished with equilibrium (   37) arag = Cc(AE)(cc)
Testing divariant assemblage      5,      5 assemblages remaining to be tested.
Testing divariant assemblage      6,      6 assemblages remaining to be tested.
finished with equilibrium (   38) Do(AE)(cc_49.0) = Cc(AE)(mag_96.4) Do(AE)(cc_51.0)
Testing divariant assemblage      7,      7 assemblages remaining to be tested.
Testing divariant assemblage      8,      6 assemblages remaining to be tested.
Testing divariant assemblage      9,      7 assemblages remaining to be tested.
Testing divariant assemblage     10,      6 assemblages remaining to be tested.
Testing divariant assemblage     11,      6 assemblages remaining to be tested.
Testing divariant assemblage     12,      7 assemblages remaining to be tested.
Testing divariant assemblage     13,      6 assemblages remaining to be tested.
finished with equilibrium (   39) Cc(AE)(mag_96.4) Do(AE)(cc_51.0) = Cc(AE)(mag_94.4)
Testing divariant assemblage     14,      9 assemblages remaining to be tested.
Testing divariant assemblage     15,      8 assemblages remaining to be tested.
Testing divariant assemblage     16,      7 assemblages remaining to be tested.
Testing divariant assemblage     17,      8 assemblages remaining to be tested.
Testing divariant assemblage     18,      8 assemblages remaining to be tested.
Testing divariant assemblage     19,      9 assemblages remaining to be tested.
Testing divariant assemblage     20,      8 assemblages remaining to be tested.
finished with equilibrium (   40) Cc(AE)(mag_94.4) Do(AE)(cc_51.0) = Cc(AE)(mag_92.3)
Testing divariant assemblage     21,     10 assemblages remaining to be tested.
```

```
Testing divariant assemblage    22,     9 assemblages remaining to be tested.
Testing divariant assemblage    23,     8 assemblages remaining to be tested.
Testing divariant assemblage    24,     7 assemblages remaining to be tested.
Testing divariant assemblage    25,     8 assemblages remaining to be tested.
Testing divariant assemblage    26,     7 assemblages remaining to be tested.
Testing divariant assemblage    27,     7 assemblages remaining to be tested.
Testing divariant assemblage    28,     7 assemblages remaining to be tested.
Testing divariant assemblage    29,     6 assemblages remaining to be tested.
finished with equilibrium (    41) Cc(AE)(mag_92.3) Do(AE)(cc_51.0) = Cc(AE)(mag_90.3)
Testing divariant assemblage    30,     8 assemblages remaining to be tested.
Testing divariant assemblage    31,     7 assemblages remaining to be tested.
Testing divariant assemblage    32,     7 assemblages remaining to be tested.
Testing divariant assemblage    33,     7 assemblages remaining to be tested.
Testing divariant assemblage    34,     8 assemblages remaining to be tested.
Testing divariant assemblage    35,     8 assemblages remaining to be tested.
Testing divariant assemblage    36,     7 assemblages remaining to be tested.
finished with equilibrium (    42) Cc(AE)(mag_90.3) Do(AE)(cc_51.0) = Cc(AE)(mag_88.2)
Testing divariant assemblage    37,     9 assemblages remaining to be tested.
Testing divariant assemblage    38,     8 assemblages remaining to be tested.
Testing divariant assemblage    39,     8 assemblages remaining to be tested.
Testing divariant assemblage    40,     7 assemblages remaining to be tested.
Testing divariant assemblage    41,     6 assemblages remaining to be tested.
Testing divariant assemblage    42,     5 assemblages remaining to be tested.
Testing divariant assemblage    43,     6 assemblages remaining to be tested.
Testing divariant assemblage    44,     6 assemblages remaining to be tested.
finished with equilibrium (    43) Cc(AE)(mag_88.2) Do(AE)(cc_51.0) = Cc(AE)(mag_86.2)
Testing divariant assemblage    45,     8 assemblages remaining to be tested.
Testing divariant assemblage    46,     7 assemblages remaining to be tested.
Testing divariant assemblage    47,     6 assemblages remaining to be tested.
Testing divariant assemblage    48,     6 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.
**warning ver066** Metastable assemblage into FLIPIT:
    mag_86.2 cc_51.0
v = 5000.00     1255.50     1.00000     0.00000     0.00000
Testing divariant assemblage    52,     6 assemblages remaining to be tested.
**warning ver066** Metastable assemblage into FLIPIT:
    mag_86.2 mag_88.2
v = 5000.00     1255.50     1.00000     0.00000     0.00000
Testing divariant assemblage    53,     5 assemblages remaining to be tested.
Testing divariant assemblage    54,     5 assemblages remaining to be tested.
Testing divariant assemblage    55,     4 assemblages remaining to be tested.
Testing divariant assemblage    56,     4 assemblages remaining to be tested.
Testing divariant assemblage    57,     5 assemblages remaining to be tested.
Testing divariant assemblage    58,     4 assemblages remaining to be tested.
Testing divariant assemblage    59,     4 assemblages remaining to be tested.
Testing divariant assemblage    60,     4 assemblages remaining to be tested.
Testing divariant assemblage    61,     3 assemblages remaining to be tested.
Testing divariant assemblage    62,     3 assemblages remaining to be tested.
Testing divariant assemblage    63,     4 assemblages remaining to be tested.
```

```
Testing divariant assemblage    64,    4 assemblages remaining to be tested.
Testing divariant assemblage    65,    3 assemblages remaining to be tested.
Testing divariant assemblage    66,    2 assemblages remaining to be tested.
Testing divariant assemblage    67,    3 assemblages remaining to be tested.
Testing divariant assemblage    68,    3 assemblages remaining to be tested.
Testing divariant assemblage    69,    2 assemblages remaining to be tested.
finished with equilibrium (    44) Cc(AE)(mag_16.4) Do(AE)(cc_55.1) = Cc(AE)(mag_18.5)
Testing divariant assemblage    70,    4 assemblages remaining to be tested.
Testing divariant assemblage    71,    4 assemblages remaining to be tested.
Testing divariant assemblage    72,    3 assemblages remaining to be tested.
finished with equilibrium (    45) Cc(AE)(mag_18.5) Do(AE)(cc_55.1) = Do(AE)(cc_57.2)
Testing divariant assemblage    73,    5 assemblages remaining to be tested.
Testing divariant assemblage    74,    4 assemblages remaining to be tested.
Testing divariant assemblage    75,    4 assemblages remaining to be tested.
**warning ver066** Metastable assemblage into FLIPIT:
   mag_16.4 arag
v = 30000.0     1150.50     1.00000     0.00000     0.00000
Testing divariant assemblage    76,    3 assemblages remaining to be tested.
Testing divariant assemblage    77,    2 assemblages remaining to be tested.
finished with equilibrium (    46) Do(AE)(cc_57.2) Cc(AE)(mag_18.5) = Cc(AE)(mag_20.5)
Testing divariant assemblage    78,    4 assemblages remaining to be tested.
Testing divariant assemblage    79,    4 assemblages remaining to be tested.
Testing divariant assemblage    80,    4 assemblages remaining to be tested.
Testing divariant assemblage    81,    3 assemblages remaining to be tested.
Testing divariant assemblage    82,    3 assemblages remaining to be tested.
Testing divariant assemblage    83,    3 assemblages remaining to be tested.
Testing divariant assemblage    84,    3 assemblages remaining to be tested.
Testing divariant assemblage    85,    2 assemblages remaining to be tested.
Testing divariant assemblage    86,    2 assemblages remaining to be tested.
Testing divariant assemblage    87,    2 assemblages remaining to be tested.
Testing divariant assemblage    88,    2 assemblages remaining to be tested.
Testing divariant assemblage    89,    2 assemblages remaining to be tested.
Testing divariant assemblage    90,    1 assemblages remaining to be tested.
Testing divariant assemblage    91,    0 assemblages remaining to be tested.

Compositions for simplicial model: Do(AE)
             Minimum       Maximum
   cc         0.49000       0.57167
   mag          0.42833       0.51000
Compositions for simplicial model: Cc(AE)
             Minimum       Maximum
   mag          0.20521E-01    0.98500
   cc         0.15000E-01    0.97948
```

(3) Plotting the calculated phase diagram (PSVDRAW)

Run PSWDRAW to plot the calculated pseudosection:

```
C:\PERPLEX\Perplex7110>psvdraw
Perple_X release 7.1.10 Dec 21, 2024.
```

```
Copyright (C) 1986-2024 James A D Connolly <www.perplex.ethz.ch/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)
   contour_t_interval       50.00    >0 [50.0]
   contour_p_interval     1000.00    >0 [1000.0]
   field_fill           T         [T] F
   field_label           T         [T] F
   numeric_field_label    F         [F] T, if T PSSECT writes list to *_assemblages.txt
   replicate_label       0.250      0->1 [0.025]
   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
   splines              T         [T] F
   tenth_ticks           F         [F] T
   text_scale           1.000      [1.] (rel)
   plot_extra_data       F         [T] F, to plot, e.g., experimental observations
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:
   - field labeling
   - 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.

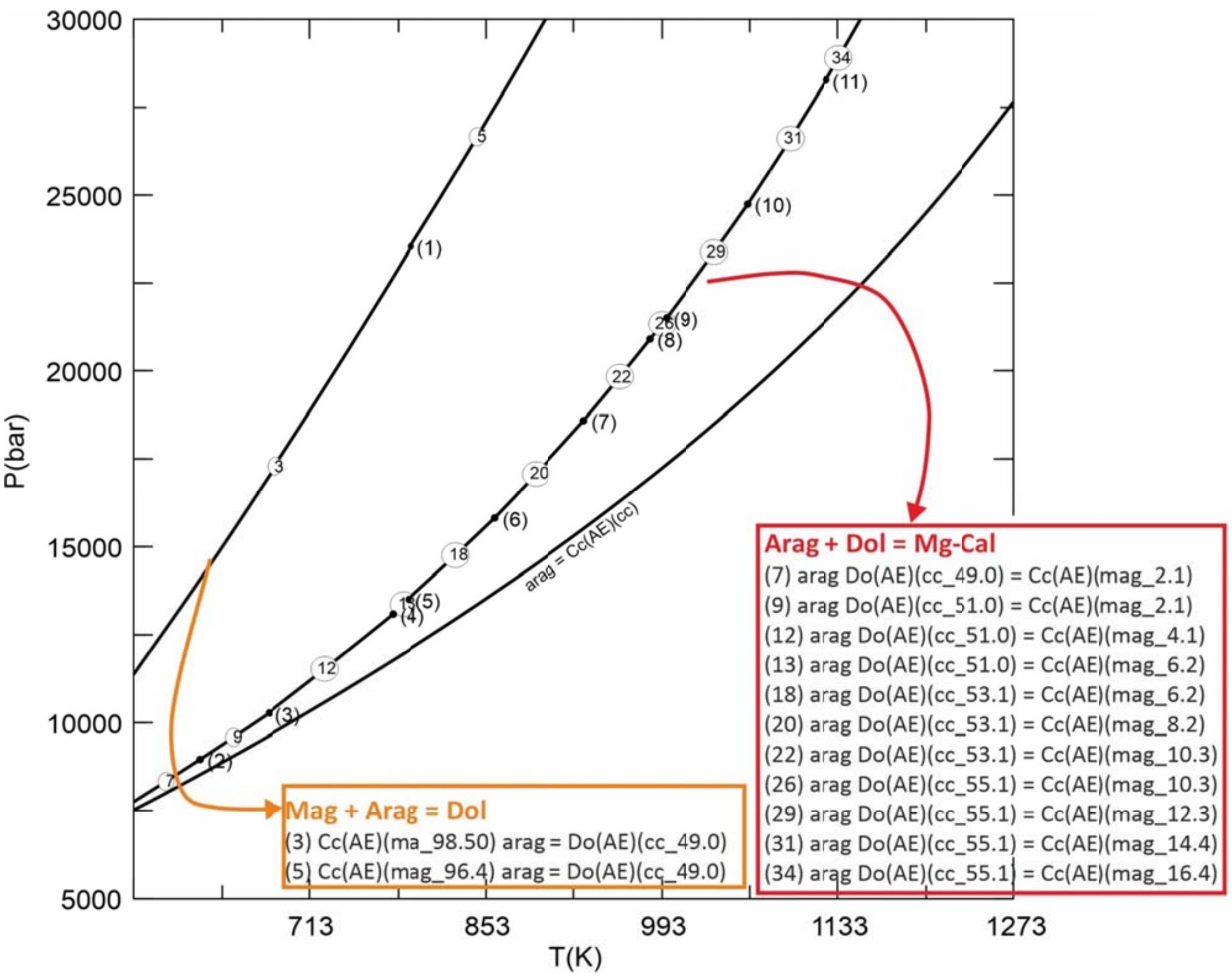
0

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

```
(3) Cc(AE)(ma_98.50) arag = Do(AE)(cc_49.0)
(5) Cc(AE)(mag_96.4) arag = Do(AE)(cc_49.0)
```

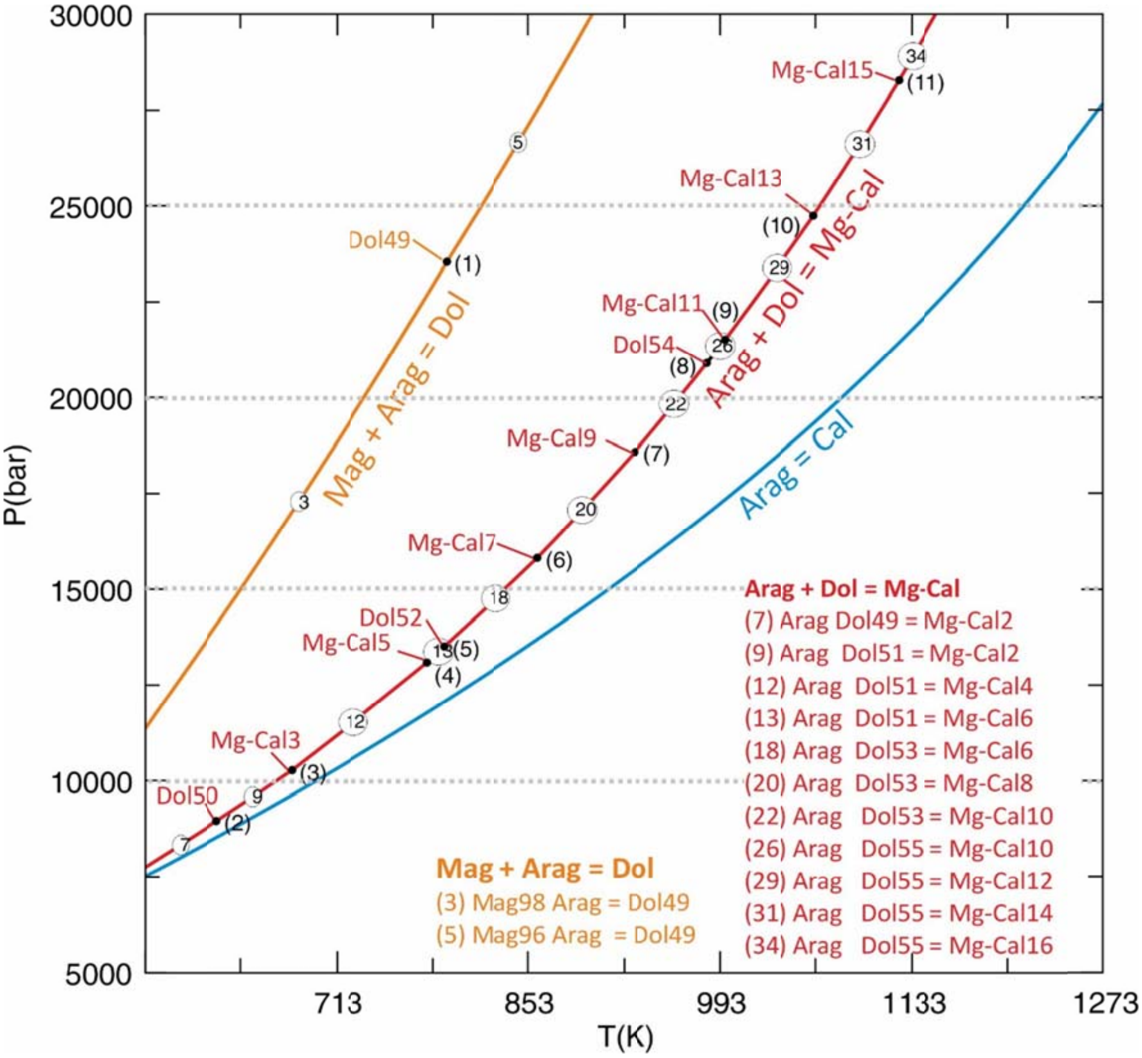
Arag + Dol = Mg-Cal

```
(7) arag Do(AE)(cc_49.0) = Cc(AE)(mag_2.1)
(9) arag Do(AE)(cc_51.0) = Cc(AE)(mag_2.1)
(12) arag Do(AE)(cc_51.0) = Cc(AE)(mag_4.1)
(13) arag Do(AE)(cc_51.0) = Cc(AE)(mag_6.2)
(18) arag Do(AE)(cc_53.1) = Cc(AE)(mag_6.2)
(20) arag Do(AE)(cc_53.1) = Cc(AE)(mag_8.2)
(22) arag Do(AE)(cc_53.1) = Cc(AE)(mag_10.3)
(26) arag Do(AE)(cc_55.1) = Cc(AE)(mag_10.3)
(29) arag Do(AE)(cc_55.1) = Cc(AE)(mag_12.3)
(31) arag Do(AE)(cc_55.1) = Cc(AE)(mag_14.4)
(34) arag Do(AE)(cc_55.1) = Cc(AE)(mag_16.4)
```

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

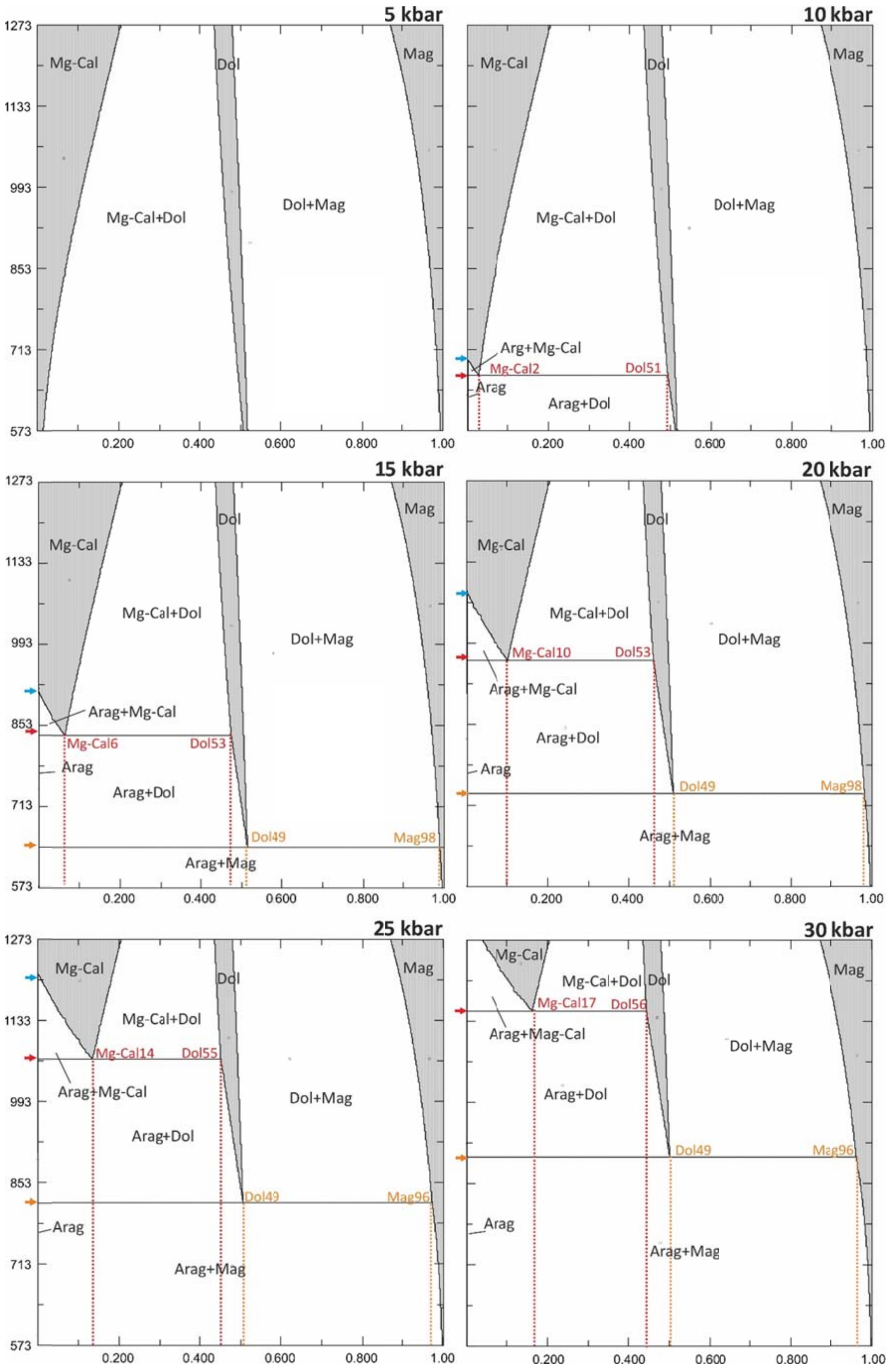
You can now compare the P-T projection with the T-XMgO sections obtained in Ex. 6.



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
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
10 kbar
Mg-Cal
Dol
Mag
Mg-Cal+Dol
Dol+Mag
Arg+Mg-Cal
Mg-Cal2
Dol51
Arag
Arag+Dol
15 kbar
Mg-Cal
Dol
Mag
Mg-Cal+Dol
Dol+Mag
Arag+Mg-Cal
Mg-Cal6
Dol53
Arag
Arag+Dol
Dol49
Mag98
Arag+Mag
20 kbar
Mg-Cal
Dol
Mag
Mg-Cal+Dol
Dol+Mag
Mg-Cal10
Dol53
Arag+Mg-Cal
Arag+Dol
Arag
Dol49
Mag98
Arag+Mag
25 kbar
Mg-Cal
Dol
Mag
Mg-Cal+Dol
Mg-Cal14
Dol55
Arag+Mg-Cal
Dol+Mag
Arag+Dol
Dol49
Mag96
Arag
Arag+Mag
30 kbar
Mg-Cal
Mg-Cal+Dol
Dol
Mag
Mg-Cal17
Dol56
Arag+Mag-Cal
Dol+Mag
Arag+Dol
Dol49
Mag96
Arag
Arag+Mag

Ex 8

Ex. 8 – AFM chemographic diagrams 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 H_2O, SiO_2 (q), KAl_3O_5 (mu) into the sub-composition MgO-FeO-Al_2O_3.

(1) Projection through muscovite implies that **a muscovite component must be defined (MU = 0.5 K_2O + 1.5 Al_2O_3)**. Along the KAl_3O_5-SiO_2 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 – 0.5Al_2O_3)** and **ANN (= 1.5 FeO – 0.5Al_2O_3)**, 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\Perplex7110>build

Perple_X release 7.1.10 Dec 21, 2024.
Copyright (C) 1986-2024 James A D Connolly <www.perplex.ethz.ch/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 = hp62ver.dat]:
enter

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)?
y
```

Three new components should be defined here:

MU = 0.5 K_2O + 1.5 Al_2O_3

PHL = 3 MgO - Al_2O_3

ANN (=3 FeO - Al_2O_3)

MU will be defined by replacing the normal K_2O 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 (< 13) in MU    1 per line, <enter> to finish:
Al2O3

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

Muscovite has the formula: $KAl_3Si_3O_{10}(OH)_2$; if SiO_2 and H_2O are considered in excess, its composition is defined by 0.5 K_2O + 1.5 Al_2O_3 (KAl_3O_5)

```
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 K_2O 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 (< 13) in PHL   1 per line, <enter> to finish:
Al2O3

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

Phlogopite has the formula: $KMg_3AlSi_3O_{10}(OH)_2$. Considering H_2O, SiO_2 and KAl_3O_5 in excess, its composition is defined as PHL = (3MgO – Al_2O_3) or, reduced, PHL = (1.5MgO – 0.5Al_2O_3).

```
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 (< 13) 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
    6 - 0-d Infiltration-reaction-fractionation
    7 - 2-d Phase fractionation (FRAC2D and TITRATE reactive transport models)
    8 - (pseudo-)Ternary liquidus/solidus surfaces
```

```
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

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

SiO_2 and MU (KAl_3O_5) must be considered as saturated component, in this specific order.

```
**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  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:
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.

```
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*
  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
  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  - MRK DeSantis et al 1974
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
clinohumite models:      TiCh(PL)   Chum
clinoamphibole models:   cAmph_I(G) cAmph(G)   Cumm      cAmph(DP)  cAmph_I(DP
…
…
For details on these models read the commentary in solution_model.dat
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\Perplex7110>convex

Perple_X release 7.1.10 Dec 21, 2024.
Copyright (C) 1986-2024 James A D Connolly <www.perplex.ethz.ch/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: hp62ver.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: ex8_pseudocompound_glossary.txt
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        [auto] manual off
   replicate_threshold    0.1E-1     [1e-2]; static opt; <0 => no replica test
   rep_dynamic_threshold  0.1E-2     [1d-3]; dynamic opt; <0 => no replica test
   re-refine              F          [F] T
   intermediate_savrpc    F          [F] T
   intermediate_savdyn    F          [F] T
   keep_all_rpcs          T          [T] F
 Free energy minimization options:
   MINFRC_diff_increment  0.1E-6     [1e-7] 1e-3 => 1e-9
   MINFXC_solver          0          [0] >= 0 - speci2, -1 - MINFXC
   optimization_max_it    40         [40] >1
   optimization_precision 0.1E-3     [1e-4], 1e-1 => 1e-6, absolute
   dynamic_LP_start       war        [warm] cold hot
```

```
  static_LP_start        war       [hot] cold warm
  order_check            F         [F] T
  refinement_points       5        [auto] 1->14
  scatter-points         T         [T] F
  scatter-increment      0.1E-1    [1e-2] 1e-2 => 1e-7
  solvus_tolerance_II    aut       [0.2] 0->1
  zero_mode              0.1E-5    [1e-6] 0->1; < 0 => off
Solution subdivision options:
  initial_resolution:
    exploratory stage    0.0625     0->1 [1/16], 0 => off
    auto-refine stage    0.0063     0->1 [     ], 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:
  P_stop (bar)           0.         [0]
  PT_freeze              F          [T] F
  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]
  approx_alpha           T          [T] F
  Anderson-Gruneisen     F          [F] T
  finite_strain_alpha    F          [F] T
  speciation_precision   0.1E-4     [1d-5] <1; absolute
  speciation_max_it      100        [100]
  function_tolerance_exp 0.8        [0.8] sets x in tol = epsmch^x
  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_lagged_speciation   F          [F] T
  aq_fractionation_simpl F          [F] T
  aq_ion_H+              T          [T] F => use OH-
  aq_oxide_components    F          [F] T
  aq_solvent_solvus_tol  0.5        [0.5] 0-1
  aq_vapor_epsilon       1.0        [1.]
Input/Output options:
  timing                 T          [T] F
  auto_exclude           T          [T] F
  output_iteration_detai F          [F] T
  output_iteration_g     F          [F] T
Error/warning control options:
  pause_on_error         T          [T] F
  max_warn_limit          5         [5]
  warn_interactive       T          [T] F
  aq_error_ver100        F          [F] T, abort during iteration
  aq_error_ver101        T          [T] F, solute undersaturation abort
  aq_error_ver102        T          [T] F, pure + impure solvent abort
  aq_error_ver103        T          [T] F, out-of-range HKF g abort
```

```
  aq_error_ver104       T       [T] F, abort on failed respeciation
  warning_ver637        T       [T] F
  error_ver109          T       [T] F
  do_not_reset_options   F       [F] T, prevents automatic resets
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    cfsg     mfpv     cmpv     cfpv     capv     fcor     hmgts    foHL     faHL     qHL
--------------------------------------------------------------------------------
--------------------------------------------------------------------------------
Summary of saturated-component entities:
 for: SiO2
  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** because the total amount of the commponents in san is <= 0 it will be rejected from this
calculation although it is a legitimate phase. To prevent this rejection transform the data base components (e.g., using
CTRANSF) so that the total amount of the components in san is > 0.

Continue execution despite this warning (Y/N)?
```

Along the KAl3O5-SiO2 join, K-feldspar has a negative composition and it is therefore rejected. This means that the calculation will only be valid within the stability field for Mu + Qz.

```
y
--------------------------------------------------------------------------------
To automatically answer interactive warnings affirmatively, set warn_interactive to false.
--------------------------------------------------------------------------------
Solution model summary:
**warning ver114** the following endmembers are missing for Chl(W):
 mnchl    ff3cli   f3clin
**warning ver102** reformulated subcomposition [M][M,T]   of Chl(W) due to missing endmembers.

  3074 pseudocompounds generated for: Chl(W)
**warning ver114** the following endmembers are missing for Gt(W):
 spss     gr      fmn_i    fkho_i   kho1     andr_i
**warning ver050** reformulating prismatic solution: Gt(W)      because of missing endmembers.
(reformulation can be controlled explicitly by excluding additional endmembers).

    16 pseudocompounds generated for: Gt(W)
**warning ver114** the following endmembers are missing for Ctd(W):
 ctdo     mnctd
    16 pseudocompounds generated for: Ctd(W)
**warning ver114** the following endmembers are missing for St(W):
 mstt     msto     mnst
    16 pseudocompounds generated for: St(W)
**warning ver114** the following endmembers are missing for Bi(W):
 mnbi     ffbi_d   fbi      ftbi_d   tbi
```

```
**warning ver102** reformulated subcomposition [M,T][M]   of Bi(W) due to missing endmembers.

    100 pseudocompounds generated for: Bi(W)
**warning ver114** the following endmembers are missing for Crd(W):
  mncrd     hmncrd_i
**warning ver050** reformulating prismatic solution: Crd(W)     because of missing endmembers.
(reformulation can be controlled explicitly by excluding additional endmembers).

    286 pseudocompounds generated for: Crd(W)
Total number of pseudocompounds:    3508

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
…
…
The following solutions were input, but are not stable:
    Ctd(W)
    Crd(W)
Compositions for prismatic model: Chl(W)
  Simplex 1
                Minimum        Maximum
    X_Mames     0.12250        0.42875
    X_Mafchl     0.0000         0.0000
    X_Mclin     0.57125        0.87750
  Simplex 2
                Minimum        Maximum
    X_Mg        0.0000        0.61250
    X_Fe       0.38750        1.0000
Compositions for simplicial model: Gt(W)
                Minimum        Maximum
    alm        0.86187       0.98500
    py        0.15000E-01    0.13813
```

```
Compositions for simplicial model: St(W)
               Minimum        Maximum
    X_mst      0.62187E-01    0.43531
    X_fst      0.56469        0.93781
Compositions for prismatic model: Bi(W)
  Simplex 1
               Minimum        Maximum
    X_Mg       0.0000         1.0000
    X_Fe       0.0000         1.0000
  Simplex 2
               Minimum        Maximum
    X_AlTs     0.0000         0.25000
    X_MBio     0.75000        1.0000
The failure rate during speciation (order-disorder) calculations is   0.000% out of a total of       9324. calculations.
Average number of iterations per speciation calculation:  5.7

**warning ver013** because the total amount of the components in san        is <= 0 it will be rejected from this
calculation although it is a legitimate phase. To prevent this rejection transform the data base components (e.g., using
CTRANSF) so that the total amount of the components in san       is > 0.

Continue execution despite this warning (Y/N)?
y
To automatically answer interactive warnings affirmatively, set warn_interactive to false.

Eliminating solution model: Ctd(W)     in auto-refinement.
Eliminating solution model: Crd(W)     in auto-refinement.
--------------------------------------------------------------------------------
Solution model summary:
   86691 pseudocompounds generated for: Chl(W)
      33 pseudocompounds generated for: Gt(W)
      82 pseudocompounds generated for: St(W)
    8422 pseudocompounds generated for: Bi(W)
Total number of pseudocompounds:   95228
Summary of included solution models:
Chl(W)    Gt(W)     St(W)     Bi(W)
--------------------------------------------------------------------------------
** Starting auto_refine computational stage **
Computing the compositional phase relations at condition  1
 cycle          1          1          1
 cycle          2          2          2
…
…
WARNING: composition of solution St(W)      has reached an internal limit (0.000)
on simplex 1 for species  1. If this warning occurs during the exploratory stage and the restriction is unintentional
then relax the limit in the solution model file and restart the calculation.
..
…
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
…
…
**warning ver991** The following solutions have compositions at an internal limit (i.e., 0<x<1):
    St(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 prismatic model: Chl(W)
  Simplex 1
               Minimum       Maximum
    X_Mames     0.11025       0.41650
    X_Mafchl    0.0000        0.0000
    X_Mclin    0.58350       0.88975
  Simplex 2
               Minimum       Maximum
    X_Mg        0.0000       0.60638
    X_Fe       0.39362       1.0000
Compositions for simplicial model: Gt(W)
               Minimum       Maximum
    alm        0.87419       0.99731
    py        0.26875E-02    0.12581
Compositions for simplicial model: St(W)
               Minimum       Maximum
    X_mst      0.31250E-03    0.42106
    X_fst      0.57894       0.99969
Compositions for prismatic model: Bi(W)
  Simplex 1
               Minimum       Maximum
    X_Mg        0.0000        1.0000
    X_Fe       0.0000        1.0000
  Simplex 2
               Minimum       Maximum
    X_AlTs      0.0000       0.26119
    X_MBio     0.73881        1.0000
The failure rate during speciation (order-disorder) calculations is   0.000% out of a total of     355004. calculations.
Average number of iterations per speciation calculation:  4.2
```

(3) Plotting the calculated phase diagram (PSVDRAW)

Run PSWDRAW to plot the calculated pseudosection:

```
C:\PERPLEX\Perplex7110>psvdraw

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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)
   contour_t_interval      50.00    >0 [50.0]
   contour_p_interval    1000.00    >0 [1000.0]
   field_fill            T        [T] F
   field_label           T        [T] F
   numeric_field_label    F        [F] T, if T PSSECT writes list to *_assemblages.txt
   replicate_label      0.250      0->1 [0.025]
   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
   splines              T        [T] F
   tenth_ticks          F        [F] T
   text_scale           1.000      [1.] (rel)
   plot_extra_data       F        [T] F, to plot, e.g., experimental observations
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
```
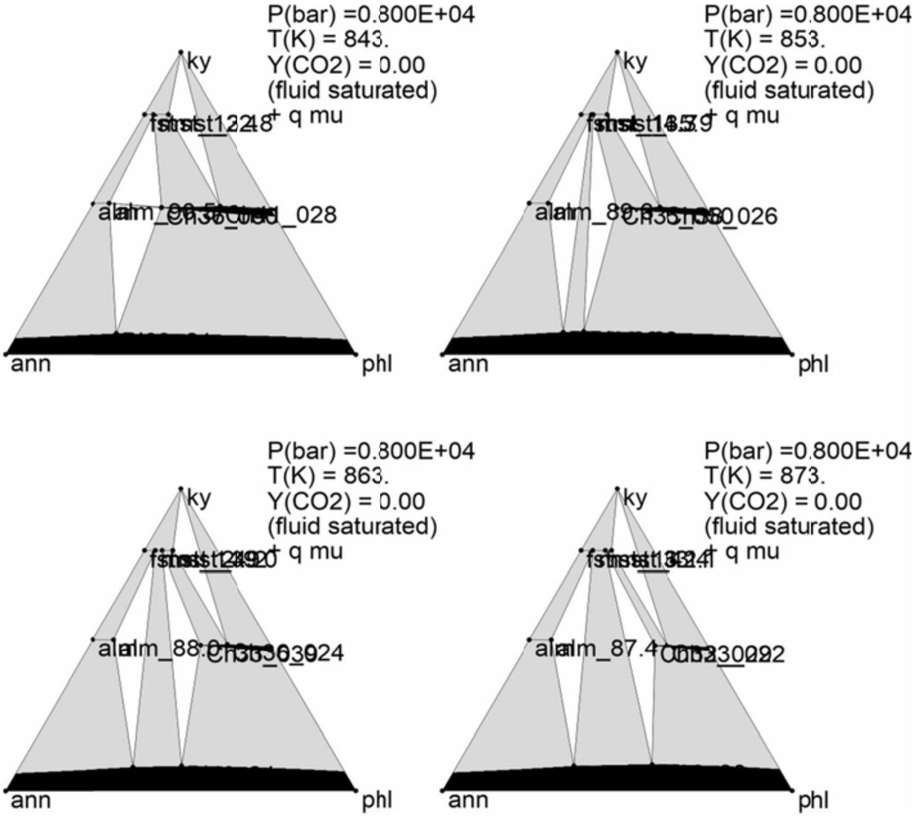
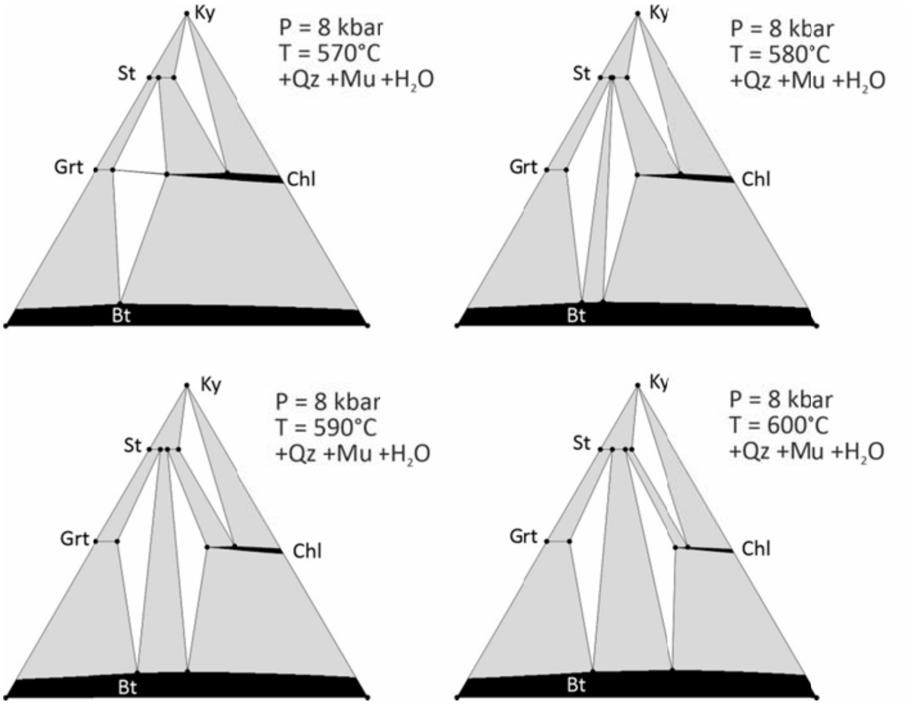



In the resulting diagrams white fields are three-phases fields (+Qz+Mu+H2O), grey fields are two-phases fields (+Qz+Mu+H2O) and black fields are one-phase fields (+Qz+Mu+H2O).



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\Perplex7110>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]:
ex9

The problem definition file will be named: ex9.dat

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

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
    6 - 0-d Infiltration-reaction-fractionation
    7 - 2-d Phase fractionation (FRAC2D and TITRATE reactive transport models)
    8 - (pseudo-)Ternary liquidus/solidus surfaces
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 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:
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 ZnO
Enter names, 1 per line, press <enter> to finish:
MgO
Al2O3
K2O
```

```
FeO

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*
  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
  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  - MRK DeSantis et al 1974
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         20      20       20 x  20 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:
 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 the solution model file name [default = solution_model.dat]:
[enter]
…

Select models from the following list, enter 1 per line, press <enter> to finish
clinohumite models:      TiCh(PL)   Chum
clinoamphibole models:    cAmph_I(G) cAmph(G)   Cumm      cAmph(DP)  cAmph_I(DP
…
For details on these models read the commentary in solution_model.dat
```

```
Chl(W)
Bi(W)
Gt(W)
Ctd(W)
St(W)
Crd(W)

Enter calculation title:
Ex9
```

(2) Doing the calculation (VERTEX)

Run VERTEX to make the calculation:

```
C:\PERPLEX\Perplex7110>vertex

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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: hp62ver.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: not requested
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      [auto] manual off
   replicate_threshold    0.1E-1    [1e-2]; static opt; <0 => no replica test
   rep_dynamic_threshold   0.1E-2    [1d-3]; dynamic opt; <0 => no replica test
   re-refine             F        [F] T
   intermediate_savrpc    F        [F] T
   intermediate_savdyn    F        [F] T
   keep_all_rpcs         T        [T] F
  Free energy minimization options:
   MINFRC_diff_increment   0.1E-6    [1e-7] 1e-3 => 1e-9
   MINFXC_solver          0       [0] >= 0 - speci2, -1 - MINFXC
   optimization_max_it    40       [40] >1
   optimization_precision  0.1E-3    [1e-4], 1e-1 => 1e-6, absolute
   dynamic_LP_start       war      [warm] cold hot
   static_LP_start       war      [hot] cold warm
```

```
  order_check            F        [F] T
  refinement_points       6       [auto] 1->14
  scatter-points         T        [T] F
  scatter-increment      0.1E-1    [1e-2] 1e-2 => 1e-7
  solvus_tolerance_II    aut      [0.2] 0->1
  zero_mode              0.1E-5    [1e-6] 0->1; < 0 => off
2D grid options:
  x_nodes              20 / 60   [20/40] >0, <2048; effective x-resolution   20 / 473 nodes
  y_nodes              20 / 60   [20/40] >0, <2048; effective y-resolution   20 / 473 nodes
  grid_levels           1 / 4     [1/4] >0, <10
  linear_model           on       [on] off
Solution subdivision options:
  initial_resolution:     0.2000    [1/5] 0->1; 0 => off
  stretch_factor         0.0020    [2d-3] >0
  non_linear_switch       F        [F] T
  subdivision_override    off      [lin] off str
  refine_endmembers       F        [F] T
Thermodynamic options:
  P_stop (bar)           0.       [0]
  PT_freeze              F        [T] F
  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]
  approx_alpha           T        [T] F
  Anderson-Gruneisen     F        [F] T
  finite_strain_alpha    F        [F] T
  speciation_precision    0.1E-4    [1d-5] <1; absolute
  speciation_max_it       100      [100]
  function_tolerance_exp  0.8      [0.8] sets x in tol = epsmch^x
  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_lagged_speciation    F        [F] T
  aq_fractionation_simpl  F        [F] T
  aq_ion_H+              T        [T] F => use OH-
  aq_oxide_components     F        [F] T
  aq_solvent_solvus_tol   0.5      [0.5] 0-1
  aq_vapor_epsilon       1.0      [1.]
Input/Output options:
  timing                T        [T] F
  auto_exclude           T        [T] F
  output_iteration_detai  F        [F] T
  output_iteration_g      F        [F] T
  logarithmic_p          F        [F] T
  logarithmic_X          F        [F] T
  bad_number             NaN      [NaN]
  interim_results        aut      [auto] off manual
Information file output options:
  option_list_files       F        [F] T; echo computational options
  pseudocompound_file     T        [F] T; echo static pseudocompound compositions
  auto_refine_file        F        [T] F; echo auto-refine compositions
```

```
    seismic_data_file       T         [F] T; echo seismic wavespeed options
  Error/warning control options:
    pause_on_error          T         [T] F
    max_warn_limit            5       [5]
    warn_interactive        T         [T] F
    aq_error_ver100         F         [F] T, abort during iteration
    aq_error_ver101         T         [T] F, solute undersaturation abort
    aq_error_ver102         T         [T] F, pure + impure solvent abort
    aq_error_ver103         T         [T] F, out-of-range HKF g abort
    aq_error_ver104         T         [T] F, abort on failed respeciation
    warning_ver637          T         [T] F
    error_ver109          T         [T] F
    do_not_reset_options    F         [F] T, prevents automatic resets
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    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      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 ver102** reformulated subcomposition [M][M,T]   of Chl(W) due to missing endmembers.
     122 pseudocompounds generated for: Chl(W)
**warning ver114** the following endmembers are missing for Gt(W):
  spss     gr       fmn_i    fkho_i   kho1     andr_i
**warning ver050** reformulating prismatic solution: Gt(W)      because of missing endmembers.
(reformulation can be controlled explicitly by excluding additional endmembers).
       4 pseudocompounds generated for: Gt(W)
**warning ver114** the following endmembers are missing for Ctd(W):
  ctdo     mnctd
       4 pseudocompounds generated for: Ctd(W)
**warning ver114** the following endmembers are missing for St(W):
  mstt     msto     mnst
       4 pseudocompounds generated for: St(W)
**warning ver114** the following endmembers are missing for Bi(W):
  mnbi     ffbi_d   fbi      ftbi_d   tbi
**warning ver102** reformulated subcomposition [M,T][M]   of Bi(W) due to missing endmembers.
      16 pseudocompounds generated for: Bi(W)
**warning ver114** the following endmembers are missing for Crd(W):
  mncrd    hmncrd_i
**warning ver050** reformulating prismatic solution: Crd(W)     because of missing endmembers.
(reformulation can be controlled explicitly by excluding additional endmembers).
      33 pseudocompounds generated for: Crd(W)
```

```
Total number of pseudocompounds:     183

Summary of included solution models:
Chl(W)    Gt(W)     Ctd(W)    St(W)     Bi(W)     Crd(W)
------------------------------------------------------------------------------
** Starting exploratory computational stage **
100.0% done with low level grid.
------------------------------------------------------------------------------
Exploratory stage generated:
     77 compositions for: Chl(W)
     13 compositions for: Gt(W)
      9 compositions for: Ctd(W)
     21 compositions for: St(W)
    172 compositions for: Bi(W)
     65 compositions for: Crd(W)
Total number of compositions:     357
------------------------------------------------------------------------------
------------------------------------------------------------------------------
** Starting auto-refine computational stage **
100.0% done with low level grid.

Beginning grid refinement stage.
   588 grid cells to be refined at grid level 2
      ...working (   501 minimizations done)
      ...working (  1002 minimizations done)
      refinement at level 2 involved   1253 minimizations
  4853 minimizations required of the theoretical limit of   14161
  1044 grid cells to be refined at grid level 3
      ...working (   252 minimizations done)
      ...working (   753 minimizations done)
      ...working (  1254 minimizations done)
      ...working (  1757 minimizations done)
      refinement at level 3 involved   1909 minimizations
  6762 minimizations required of the theoretical limit of   56169
  1768 grid cells to be refined at grid level 4
      ...working (   350 minimizations done)
      ...working (   852 minimizations done)
      ...working (  1354 minimizations done)
      ...working (  1856 minimizations done)
      ...working (  2357 minimizations done)
      ...working (  2858 minimizations done)
      refinement at level 4 involved   2964 minimizations
  9726 minimizations required of the theoretical limit of  224676
------------------------------------------------------------------------------
    Timing                  min.        % of total
  Static G calculation      0.10260          14.9
  Dynamic G calculation     0.11745          17.0
  Static LP               0.46875E-02       0.7
  Dynamic LP              0.77865E-01      11.3
  Successive QP             0.35990         52.2
  Total of above            0.66250         96.0
```

```
 Total elapsed time       0.69010         100.0
--------------------------------------------------------------------------------
End of job: ex9
```

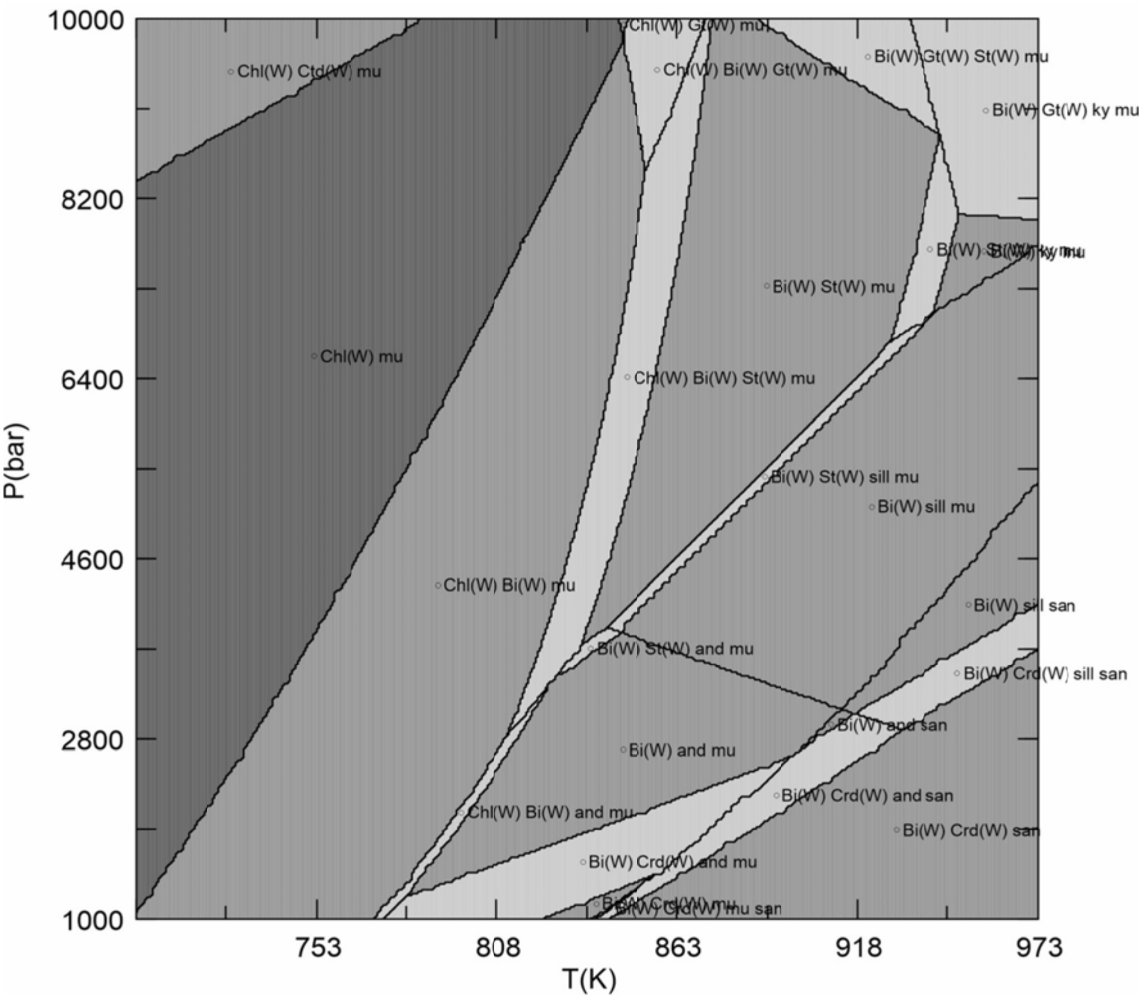
At the end of the calculation, a number of new files appear in the Perple_X folder. The most useful are the ***.prn and the ***.plt files (i.e. the text file and the plot file).

(3) Plotting the calculated phase diagram (PSSECT)

Run PSSECT to plot the calculated pseudosection:

```
C:\PERPLEX\Perplex7110>pssect

Perple_X release 7.1.10 Dec 21, 2024.
Copyright (C) 1986-2024 James A D Connolly <www.perplex.ethz.ch/copyright.html>.

Enter the project name (the name assigned in BUILD) [default = my_project]:
ex9

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)
    contour_t_interval       50.00    >0 [50.0]
    contour_p_interval     1000.00    >0 [1000.0]
    field_fill             T         [T] F
    field_label            T         [T] F
    numeric_field_label    F         [F] T, if T PSSECT writes list to *_assemblages.txt
    replicate_label        0.250      0->1 [0.025]
    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
    splines                T         [T] F
    tenth_ticks            F         [F] T
```

```
   text_scale          1.000     [1.] (rel)
   plot_extra_data       F         [T] F, to plot, e.g., experimental observations
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   2 fields for: Chl(W) Bi(W) St(W) mu
There are   5 fields for: Bi(W) Crd(W) mu san
```



Quartz and H_2O are in excess.

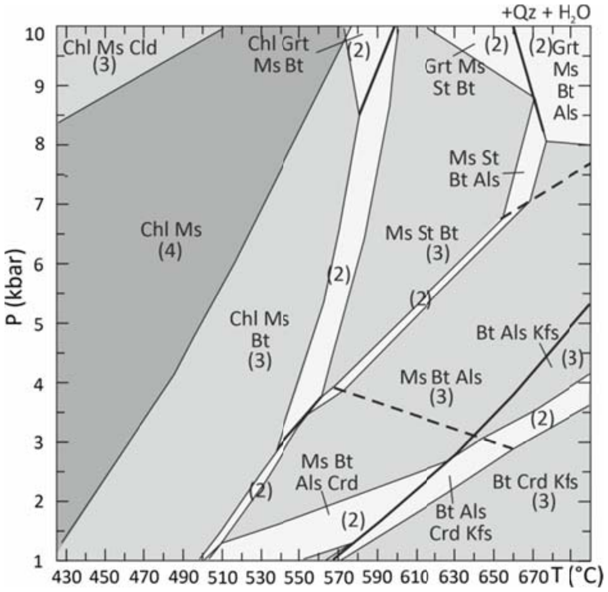
In the calculated pseudosection, field assemblages have different variances. Fields with the same grey colour have the same variance. Colour code is as follows: light grey = 2-variant fields (6 phases), medium grey = 3-variant fields (5 phases), dark grey = 4-variant fields (4 phases). Darker is the colour, higher is the variance (and lower is the number of phases!).

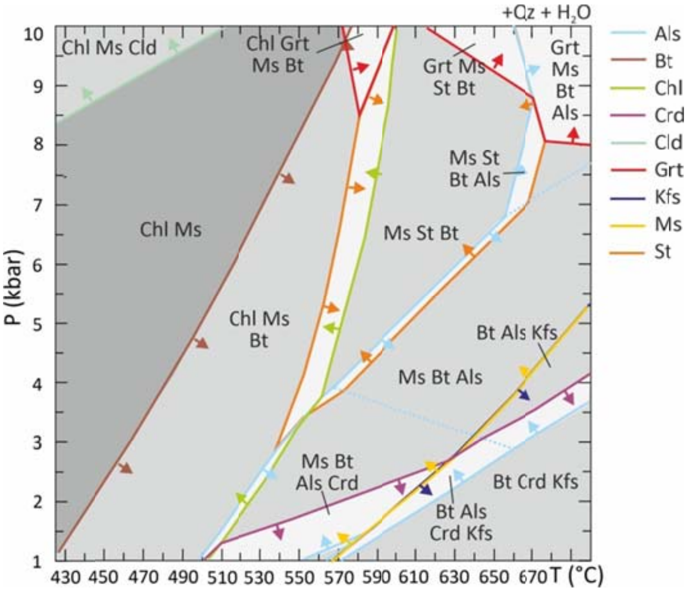
(4) PRACTICAL TIPS FOR RE-DRAWING THE PERPLE_X OUTPUTS

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**

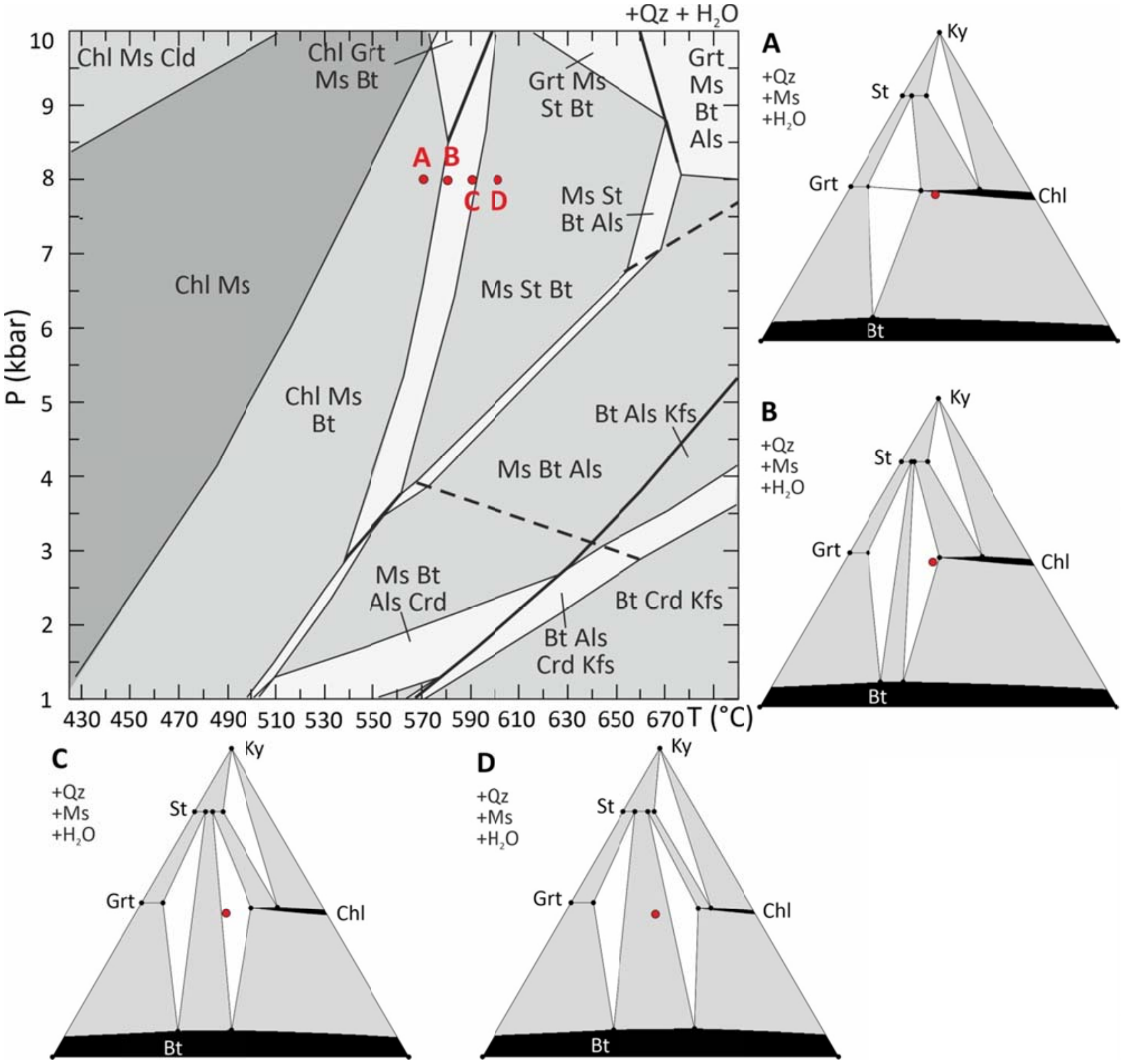




In the diagram on the left, variance of each field is reported in brackets. The thick black lines are true univariant reactions.

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\Perplex7110>werami

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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] 0-150
    aq_solvent_composition  y        [y] m: y => mol fraction, m => molality
    aq_solute_composition   m        y [m]: y => mol fraction, m => molality
    spreadsheet            T        [T] F
    logarithmic_p          F        [F] T
    logarithmic_X          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          T        [T] F
    solution_names         mod       [model] abbreviation full
    structural_formulae     T        [T] F
    output_species         T        [T] F
    output_species_props    F        [F] T
    seismic_output         som       [some] none all
    poisson_test           F        [F] T
    interim_results        aut       [auto] off manual
    sample_on_grid          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
    finite_strain_alpha     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     [2] >0
  finite_difference_p    1.0E+04  [1d4] >0; fraction = 1.0E-03  [1d-3]
 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
  fluid_shear_modulus    T       [T] F
  phi_d                  0.36    [0.36] 0->1
 Error/warning control options:
  pause_on_error         T       [T] F
  max_warn_limit         5       [5]
  warn_interactive       T       [T] F
  aq_error_ver100        F       [F] T, abort during iteration
  aq_error_ver101        T       [T] F, solute undersaturation abort
  aq_error_ver102        T       [T] F, pure + impure solvent abort
  aq_error_ver103        T       [T] F, out-of-range HKF g abort
  aq_error_ver104        T       [T] F, abort on failed respeciation
  warning_ver637         T       [T] F
  error_ver109           T       [T] F
  do_not_reset_options   F       [F] T, prevents automatic resets
To change these options see: www.perplex.ethz.ch/perplex_options.html
------------------------------------------------------------------------------
Select operational mode:
   1 - properties at specified conditions
   2 - properties on a 2d grid
   3 - properties along a 1d path
   4 - as in 3, but input from file
2

Select a property:
   1 - Specific Enthalpy (J/m3)
   2 - Density (kg/m3)
   3 - Specific heat capacity (J/K/m3)
   4 - Expansivity (1/K, for volume)
   5 - Compressibility (1/bar, for volume)
   6 - 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 an additional property or 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 an additional property or 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 an additional property or 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 an additional property or 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 an additional property or 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 an additional property or 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 an additional property or 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 an additional property or 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 an additional property or 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 an additional property or 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 an additional property or 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 [default]
   2 -  119 x  119 nodes
   3 -  237 x  237 nodes
   4 -  473 x  473 nodes
```

```
1

**warning ver178** at T(K)=   698.0     P(bar)=   1000.
the shear modulus of: Chl(W)
is missing or invalid and has been estimated with the poisson_ratio option
…
…

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%
san,vo%        ky,vo%         sill,vo%       and,vo%
min    0.588303E-001   0.814657        0.102441E-001   0.170595        0.171074E-002    7.44356         0.314547
5.63422       0.411371        0.695039       0.480096E-001
max     15.0307        42.3850        2.40039        27.4426        65.4028        57.8107        59.8453        26.2888
25.9108       29.7444       30.2407

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\Perplex7110>werami

Perple_X release 7.1.10 Dec 21, 2024.
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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] 0-150
    aq_solvent_composition  y         [y] m: y => mol fraction, m => molality
    aq_solute_composition   m         y [m]: y => mol fraction, m => molality
    spreadsheet             T         [T] F
    logarithmic_p           F         [F] T
    logarithmic_X           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           T         [T] F
    solution_names          mod       [model] abbreviation full
    structural_formulae     T         [T] F
    output_species          T         [T] F
    output_species_props    F         [F] T
    seismic_output          som       [some] none all
    poisson_test            F         [F] T
    interim_results         aut       [auto] off manual
    sample_on_grid          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
    finite_strain_alpha     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       [2] >0
    finite_difference_p     1.0E+04   [1d4] >0; fraction = 1.0E-03   [1d-3]
  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
  fluid_shear_modulus   T       [T] F
  phi_d                 0.36    [0.36] 0->1
 Error/warning control options:
  pause_on_error        T       [T] F
  max_warn_limit        5       [5]
  warn_interactive      T       [T] F
  aq_error_ver100       F       [F] T, abort during iteration
  aq_error_ver101       T       [T] F, solute undersaturation abort
  aq_error_ver102       T       [T] F, pure + impure solvent abort
  aq_error_ver103       T       [T] F, out-of-range HKF g abort
  aq_error_ver104       T       [T] F, abort on failed respeciation
  warning_ver637        T       [T] F
  error_ver109          T       [T] F
  do_not_reset_options  F       [F] T, prevents automatic resets
To change these options see: www.perplex.ethz.ch/perplex_options.html
------------------------------------------------------------------------------
Select operational mode:
    1 - properties at specified conditions
    2 - properties on a 2d grid
    3 - properties along a 1d path
    4 - as in 3, but input from file
2

Select a property:
    1 - Specific Enthalpy (J/m3)
    2 - Density (kg/m3)
    3 - Specific heat capacity (J/K/m3)
    4 - Expansivity (1/K, for volume)
    5 - Compressibility (1/bar, for volume)
    6 - 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.
Units (mass or molar) are controlled by the composition keyword in perplex_option.dat.
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.)
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 (<15)?
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          | index for MgO
1          | weighting factor for MgO

How many components in the denominator of the composition (<14)?
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 an additional property or enter 0 to finish:
8

Enter solution (left justified):
Chl(W)

Define the composition in terms of the species/endmembers of Chl(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 (<15)?
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 (<14)?
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[Chl(W)2]

Select an additional property or 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 (<15)?
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 (<14)?
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 an additional property or 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 inperplex_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 (<15)?
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 (<14)?
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 an additional property or 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 [default]
   2 -  119 x  119 nodes
   3 -  237 x  237 nodes
   4 -  473 x  473 nodes
4
**warning ver178** at T(K)=   698.0     P(bar)=   1000.
the shear modulus of: Chl(W)
is missing or invalid and has been estimated with the poisson_ratio option
…
…

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   0.118873      0.471855      0.152632      0.313717
max   0.267658      0.633967      0.335725      0.584944
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
```

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.

Pywerami can be installed as a Python package on Windows, Linux, Mac OS X, and Mac OS Apple Silicon. **You need Python 3.6 or later to run pywerami. The package requires NumPy and SciPy, and the plotting routines require Matplotlib.** You can find instructions for installing Pywerami at this link: **https://github.com/ondrolexa/pywerami**

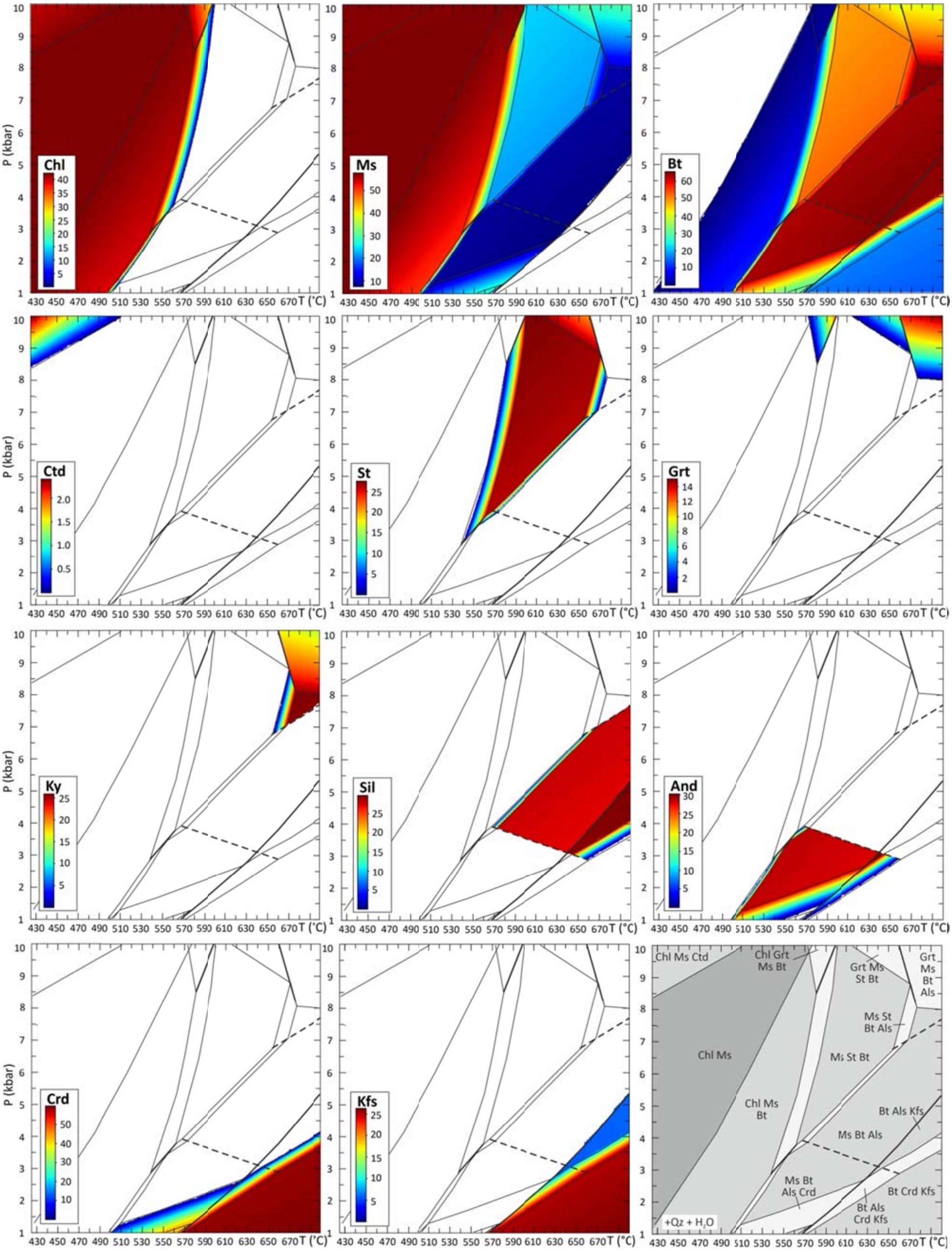
Run PYWERAMI to plot isopleths and isomodes.

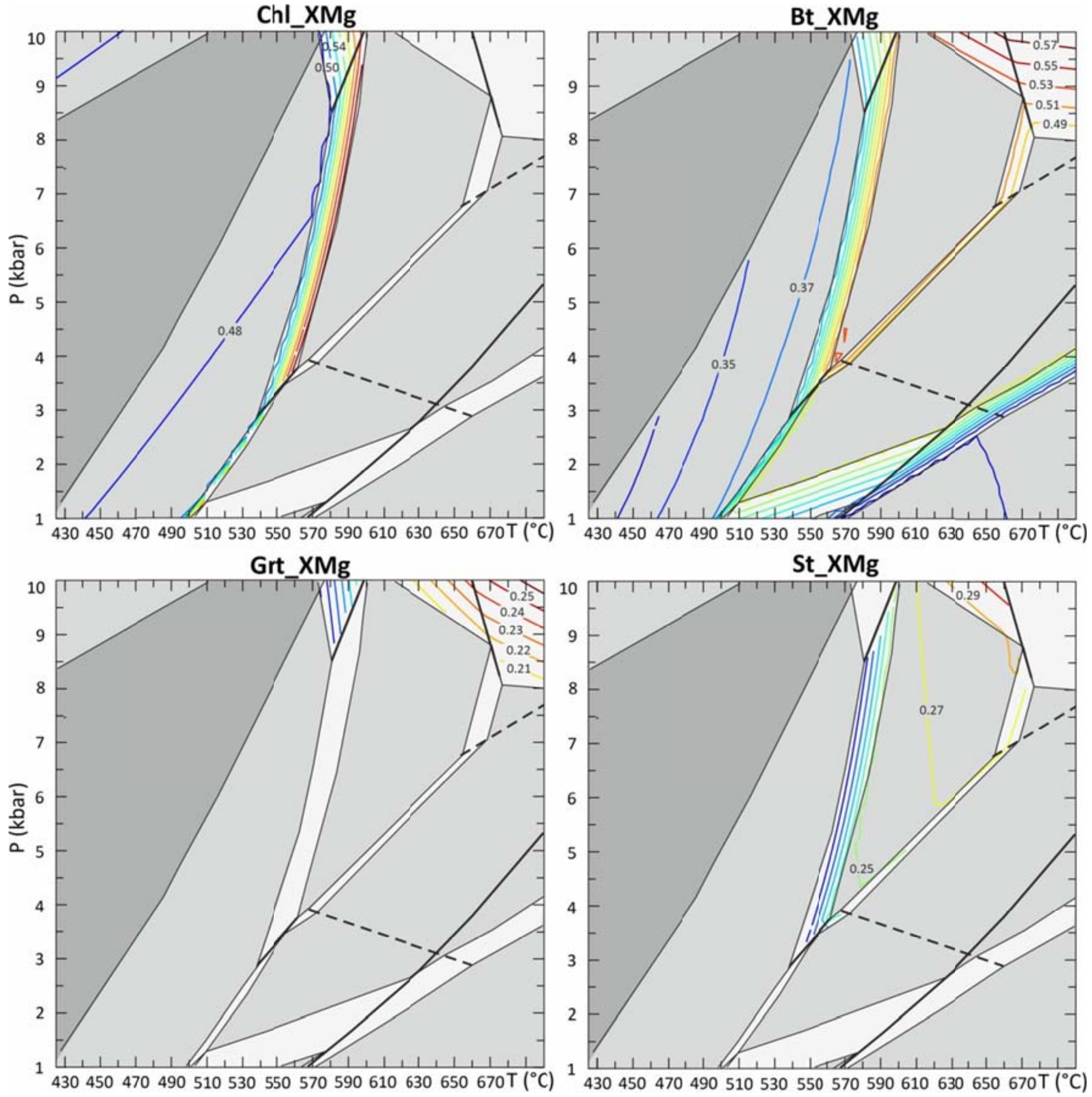
From Pywerami, open the .tab file (New).
Select the property you want to plot from the list on the left (e.g. Gt(W)vo%)

From the menu at the bottom left you can modify:
Levels: the minimum and maximum values to be plotted (Minimum/Maximum), as well as the interval between the isopleths/isomodes (using either levels or steps)
Style: the color of the lines (either Single color or Colormap; different types of Color map can be choosen using the drop-down menu), the color of the fields (filled contours); you can also add the legend (colorbar) and labelling.

You can export the image in different formats. **IF YOU WANT TO MODIFY THE FIGURE,** the best choices are .ps or .pdf.

NB: the figure below (isomodes) was obtained setting the GRID RESOLUTION to:
4 - 473 x 473 nodes


Chl
Ms
Bt
Ctd
St
Grt
Ky
Sil
And
Crd
Kfs
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
Chl Ms Ctd
Chl Grt Ms Bt
Grt Ms St Bt
Grt Ms Bt Als
Ms St Bt Als
Chl Ms
Ms St Bt
Chl Ms Bt
Bt Als Kfs
Ms Bt Als
Ms Bt Als Crd
Bt Crd Kfs
Bt Als Crd Kfs
+Qz + H₂O


Chl_XMg
Bt_XMg
Grt_XMg
St_XMg
P (kbar)
T (°C)
1
2
3
4
5
6
7
8
9
10
430 450 470 490 510 530 550 570 590 610 630 650 670
0.54
0.50
0.48
0.57
0.55
0.53
0.51
0.49
0.37
0.35
0.25
0.24
0.23
0.22
0.21
0.29
0.27
0.25

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\Perplex7110>vertex

Perple_X release 7.1.10 Dec 21, 2024.
Copyright (C) 1986-2024 James A D Connolly <www.perplex.ethz.ch/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:

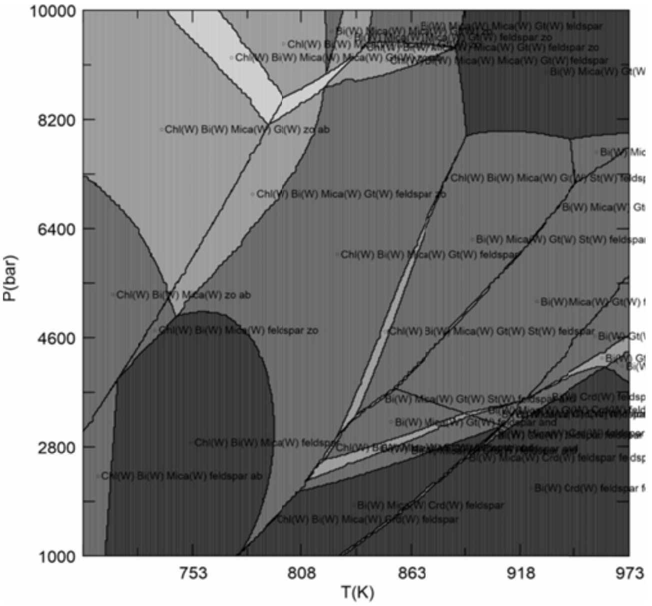
```
C:\PERPLEX\Perplex7110>pssect

Perple_X release 7.1.10 Dec 21, 2024.
Copyright (C) 1986-2024 James A D Connolly <www.perplex.ethz.ch/copyright.html>.

Enter the project name (the name assigned in BUILD) [default = my_project]:
ex10

Reading Perple_X options from: perplex_option.dat
------------------------------------------------------------------------------
Perple_X plot options are currently set as:
   Keyword:             Value:     Permitted values [default]:
   axis_label_scale       1.20       [1.2] (rel)
   bounding_box :
                          0      [0] x-min (pts)
                          0      [0] y-min (pts)
                        800      [800] x-length (pts)
                        800      [800] y-length (pts)
   contour_t_interval       50.00     >0 [50.0]
   contour_p_interval     1000.00     >0 [1000.0]
   field_fill            T         [T] F
   field_label           T         [T] F
   numeric_field_label    F         [F] T, if T PSSECT writes list to *_assemblages.txt
   replicate_label       0.250      0->1 [0.025]
   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
   splines               T         [T] F
   tenth_ticks           F         [F] T
   text_scale            1.000      [1.] (rel)
   plot_extra_data        F         [T] F, to plot, e.g., experimental observations
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
```

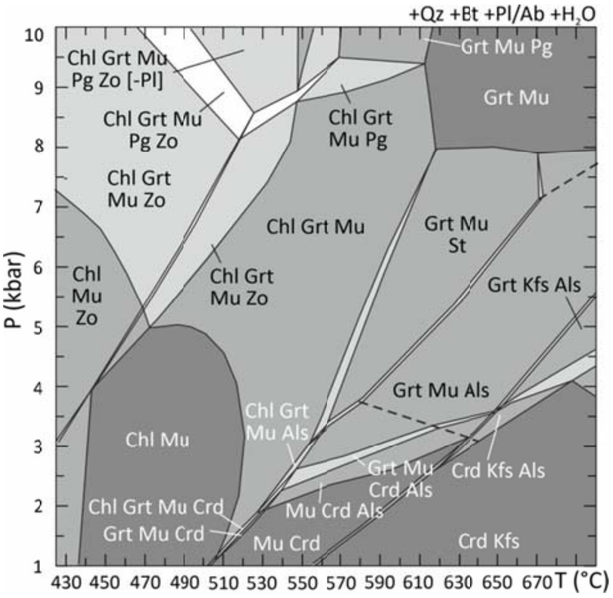
```
There are  10 fields for: Chl(W) Bi(W) Mica(W) feldspar zo ab
There are   7 fields for: Chl(W) Bi(W) Mica(W) Gt(W) feldspar zo ab
There are   2 fields for: Chl(W) Bi(W) Mica(W) Mica(W) Gt(W) feldspar zo
There are   3 fields for: Chl(W) Bi(W) Mica(W) Gt(W) feldspar and
There are  10 fields for: Chl(W) Bi(W) Mica(W) Gt(W) St(W) feldspar
There are   3 fields for: Bi(W) Mica(W) Crd(W) feldspar feldspar
There are   2 fields for: Bi(W) Mica(W) Gt(W) St(W) feldspar and
There are  11 fields for: Bi(W) Mica(W) Gt(W) St(W) feldspar sill
There are   3 fields for: Bi(W) Mica(W) Gt(W) Crd(W) feldspar sill
There are   5 fields for: Bi(W) Gt(W) Crd(W) feldspar feldspar sill
There are   6 fields for: Chl(W) Bi(W) Mica(W) Crd(W) feldspar
There are   2 fields for: Bi(W) Mica(W) Crd(W) feldspar feldspar sill
There are   6 fields for: Bi(W) Mica(W) Gt(W) feldspar feldspar sill
There are   2 fields for: Bi(W) Mica(W) Gt(W) St(W) feldspar ky
There are   2 fields for: Chl(W) Bi(W) Mica(W) Gt(W) St(W) feldspar and
```

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:

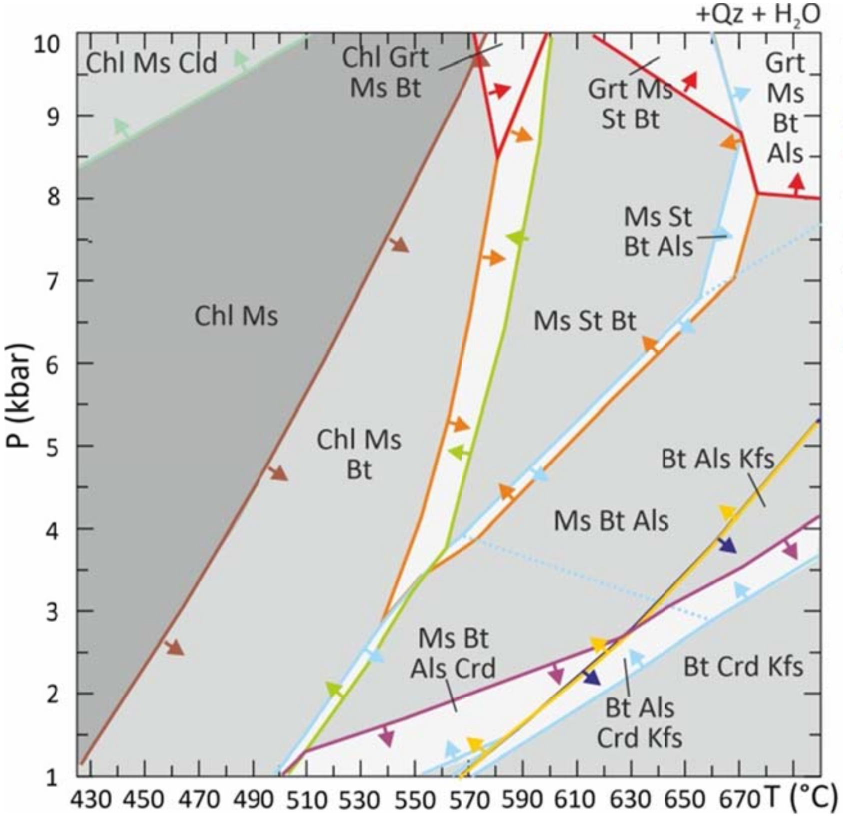
```
Stable phases at:
                  T(K)     =  753.000
                  P(bar)   =  3000.00
                  Y(CO2)   =  0.00000

Phase Compositions (molar  proportions):
             wt %     vol %    mol %    mol      Na2O     MgO      Al2O3    K2O      CaO      MnO      FeO      SiO2     H2O
 Chl(W)       17.78    17.21    10.92    4.31    0.00000  2.56857  1.22109  0.00000  0.00000  0.05786  2.15248  2.77891  4.00000
 Bi(W)        22.53    20.80    18.34    7.24    0.00000  1.12172  0.64860  0.50000  0.00000  0.02354  1.70614  2.85140  1.00000
 Mica(W)      32.05    32.30    31.02    12.3    0.06240  0.03162  1.44623  0.43623  0.00273  0.00000  0.02351  3.05240  1.00000
 feldspar     27.64    29.69    39.73    15.7    0.34064  0.00000  0.65665  0.00271  0.31330  0.00000  0.00000  2.68670  0.00000
Phase speciation (molar proportions):
 Chl(W)       mnchl: 0.01157, daph: 0.46921, ames: 0.22114, afchl: 0.19370, clin: 0.29803, och1: 0.00002, och2: -0.19367
 Bi(W)        mnbi: 0.00785, east: 0.14860, ann: 0.55017, phl: 0.23774, obi: 0.05564
 Mica(W)       mu: 0.81733, pa: 0.12480, ma1_dqf: 0.00273, cel: 0.03162, fcel: 0.02351
 feldspar     abh: 0.68127, an: 0.31330, san: 0.00543
```

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

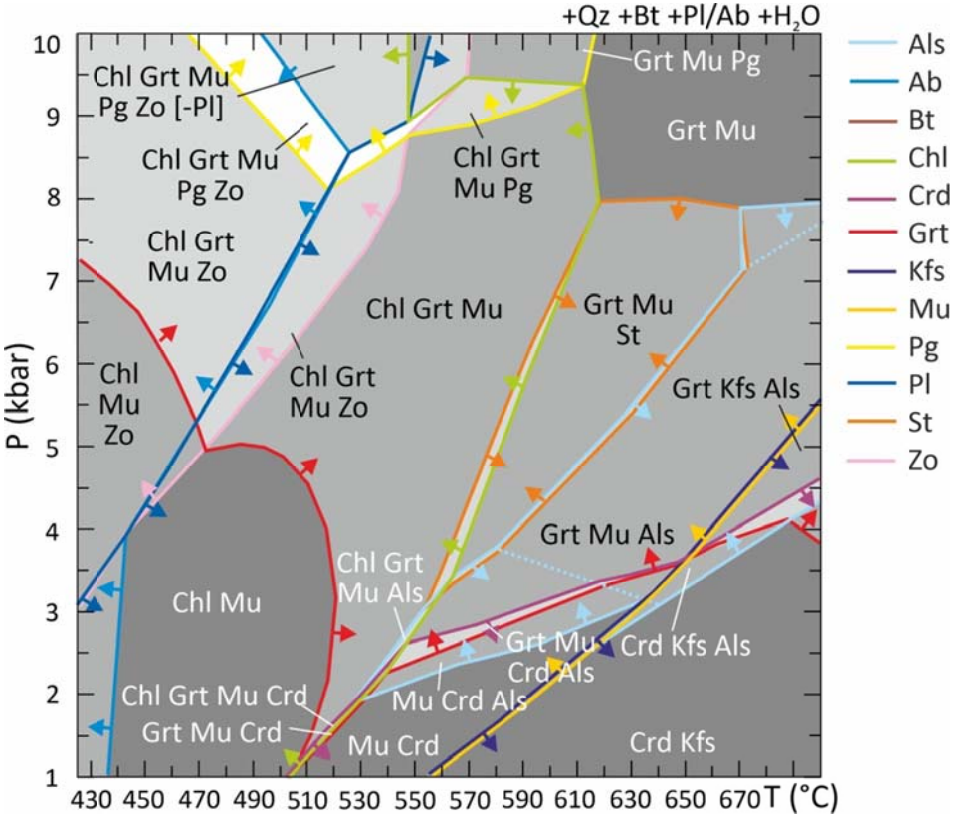

P(bar)
10000
8200
6400
4600
2800
1000
T(K)
753
808
863
918
973
Bi(W) Mica(W) Mica(W) Gt(W) feldspar
Bi(W) Mica(W) Mica(W) Gt(W) feldspar zo
Chl(W) Bi(W) Mica(W) Mica(W) Gt(W) zo ab
Mica(W) Gt(W) feldspar zo
Chl(W) Bi(W) Mica(W) Mica(W) Gt(W) feldspar
Bi(W) Mica(W) Gt(W
Chl(W) Bi(W) Mica(W) Gt(W) zo ab
Chl(W) Bi(W) Mica(W) Gt(W) feldspar zo
Chl(W) Bi(W) Mica(W) Gt(W) St(W) felds
Bi(W) Mic
Bi(W) Mica(W) Gt
Bi(W) Mica(W) Gt(W) St(W) feldspar
Chl(W) Bi(W) Mica(W) Gt(W) feldspar
Chl(W) Bi(W) Mica(W) zo ab
Bi(W) Mica(W) Gt(W) f
Chl(W) Bi(W) Mica(W) feldspar zo
Chl(W) Bi(W) Mica(W) Gt(W) St(W) feldspar
Bi(W) Gt(
Bi(W) Mica(W) Gt(W) St(W) feldspar and
Bi(W) Crd(W) feldsp
Bi(W) Mica(W) Gt(W) feldspar and
Chl(W) Bi(W) Mica(W) feldspar
Bi(W) Mica(W) Crd(W) feldspar feldsp
Chl(W) Bi(W) Mica(W) feldspar ab
Bi(W) Crd(W) feldspar f
Bi(W) Mica(W) Crd(W) feldspar
Chl(W) Bi(W) Mica(W) Crd(W) feldspar


+Qz +Bt +Pl/Ab +H$_2$O
P (kbar)
10
9
8
7
6
5
4
3
2
1
T (°C)
430
450
470
490
510
530
550
570
590
610
630
650
670
Chl Grt Mu Pg Zo [-Pl]
Chl Grt Mu Pg Zo
Grt Mu Pg
Chl Grt Mu Pg
Grt Mu
Chl Grt Mu Zo
Chl Grt Mu
Grt Mu St
Chl Mu Zo
Chl Grt Mu Zo
Grt Kfs Als
Grt Mu Als
Chl Mu
Chl Grt Mu Als
Grt Mu Crd Als
Crd Kfs Als
Chl Grt Mu Crd
Mu Crd Als
Grt Mu Crd
Mu Crd
Crd Kfs

Ex.9 (KFMASH)



Ex. 10 (MnNCKFMASH)

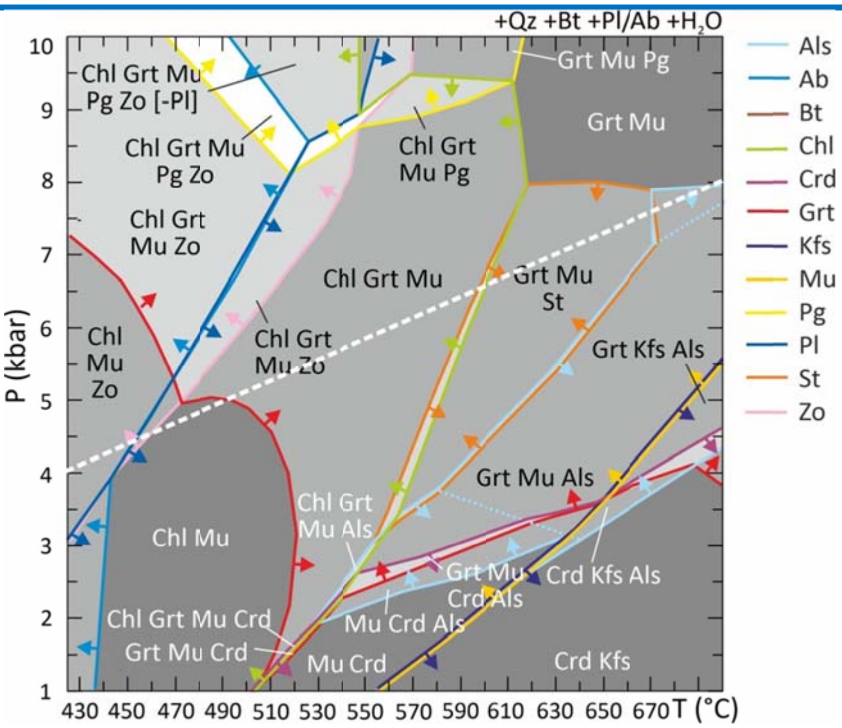


Comparing this pseudosection with that modelled in Ex. 9 (KFMASH system), it appears that the introduction of Na_2O, CaO and MnO has the following consequences:

- **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 phases (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” and put it into the Perplex7110 folder.

Run WERAMI to calculate the MODES of ALL the phases.

```
C:\PERPLEX\Perplex7110>werami

Perple_X release 7.1.10 Dec 21, 2024.
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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] 0-150
  aq_solvent_composition  y        [y] m: y => mol fraction, m => molality
  aq_solute_composition   m        y [m]: y => mol fraction, m => molality
  spreadsheet            T        [T] F
  logarithmic_p          F        [F] T
  logarithmic_X          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          T        [T] F
  solution_names         mod      [model] abbreviation full
  structural_formulae    T        [T] F
  output_species         T        [T] F
  output_species_props    F        [F] T
  seismic_output         som      [some] none all
  poisson_test           F        [F] T
  interim_results        aut      [auto] off manual
  sample_on_grid         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
  finite_strain_alpha    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      [2] >0
  finite_difference_p    1.0E+04  [1d4] >0; fraction = 1.0E-03   [1d-3]
 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
  fluid_shear_modulus    T        [T] F
  phi_d                  0.36     [0.36] 0->1
 Error/warning control options:
  pause_on_error         T        [T] F
  max_warn_limit          5       [5]
  warn_interactive       T        [T] F
```

```
  aq_error_ver100      F      [F] T, abort during iteration
  aq_error_ver101      T      [T] F, solute undersaturation abort
  aq_error_ver102      T      [T] F, pure + impure solvent abort
  aq_error_ver103      T      [T] F, out-of-range HKF g abort
  aq_error_ver104      T      [T] F, abort on failed respeciation
  warning_ver637       T      [T] F
  error_ver109       T      [T] F
  do_not_reset_options   F      [F] T, prevents automatic resets
To change these options see: www.perplex.ethz.ch/perplex_options.html
------------------------------------------------------------------------------
Select operational mode:
   1 - properties at specified conditions
   2 - properties on a 2d grid
   3 - properties along a 1d path
   4 - as in 3, but input from file
   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:
   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
```

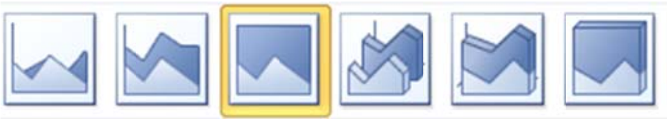
Although our aim is to calculate CUMULATIVE MODES, I suggest to not select the “cumulative mode” option here, because it is more easy to plot “normal” modes (i.e. not cumulative) using EXCEL rather than the “cumulative” modes using PSSECT.

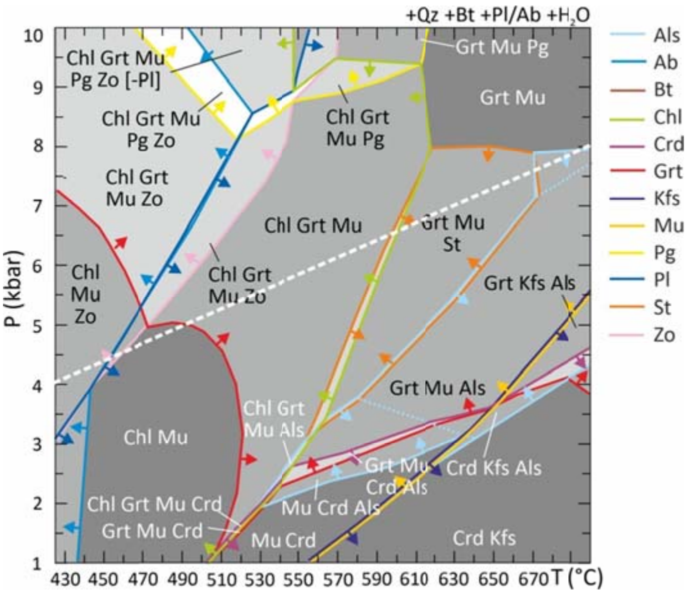
```
Include fluid in computation of aggregate (or modal) properties (y/n)?
n

**warning ver178** at T(K)=   703.0     P(bar)=   4000.
the shear modulus of: Chl(W)
is missing or invalid and has been estimated with the poisson_ratio option
...

Data ranges excluding values equal to bad_number (       NaN) specified in perplex_option.dat:
    Chl(W)        Bi(W)        Mica(W)      Mica(W)      feldspar      feldspar      ab           zo            Gt(W)         Crd(W)
and           St(W)         sill          ky
min    2.58371       13.2452       21.2761      0.100000E+100   27.9166      0.100000E+100   20.1742       0.934795E-001
0.117266E-001  0.100000E+100  0.100000E+100  0.948363      0.100000E+100  0.489876E-002
max    21.5555        37.0067        38.3934      -0.100000E+100   31.3337      -0.100000E+100   20.5352        6.29078
14.8793     -0.100000E+100 -0.100000E+100   5.72271     -0.100000E+100  0.766133
```

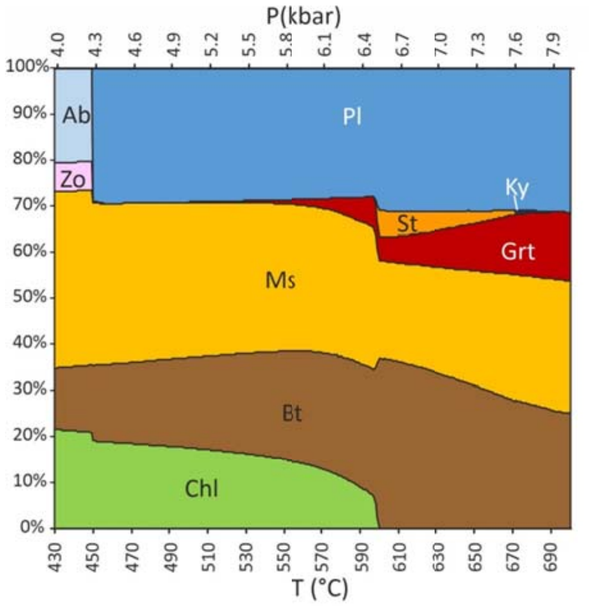
```
Output has been written to two files:
    plt format is in file: ex10_1.plt
    1d tab format is in file: ex10_1.tab
plt format files can be plotted with:
    PSVDRAW
1d tab format files can be processed with:
    PSTABLE - a Perple_X plotting program
    PERPLE_X_PLOT - a Matlab plotting script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

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\Perplex7110>build

Perple_X release 7.1.10 Dec 21, 2024.
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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 = hp62ver.dat]:
[enter]

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
    6 - 0-d Infiltration-reaction-fractionation
    7 - 2-d Phase fractionation (FRAC2D and TITRATE reactive transport models)
    8 - (pseudo-)Ternary liquidus/solidus surfaces
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 ZnO
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 ZnO
Enter names, 1 per line, press <enter> to finish:
```

```
Na2O
MgO
Al2O3
K2O
CaO
MnO
FeO

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*
  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
  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  - MRK DeSantis et al 1974
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         20      20        20 x  20 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

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
0.001
37.99
9.01
4.95
```

```
0.42
41.52

Enter the 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
0.001

Output a print file (Y/N)?
y

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 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
clinohumite models:       TiCh(PL)   Chum
ternary-feldspar models:  feldspar   feldspar_B Pl(I1,HP)  Fsp(C1)    Fsp(HGP21)
…
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\Perplex7110>vertex

Perple_X release 7.1.10 Dec 21, 2024.
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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\Perplex7110>pssect

Perple_X release 7.1.10 Dec 21, 2024.
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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
------------------------------------------------------------------------------
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)
    contour_t_interval       50.00    >0 [50.0]
    contour_p_interval     1000.00    >0 [1000.0]
    field_fill            T          [T] F
    field_label           T          [T] F
    numeric_field_label    F          [F] T, if T PSSECT writes list to *_assemblages.txt
    replicate_label       0.250      0->1 [0.025]
    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)
```
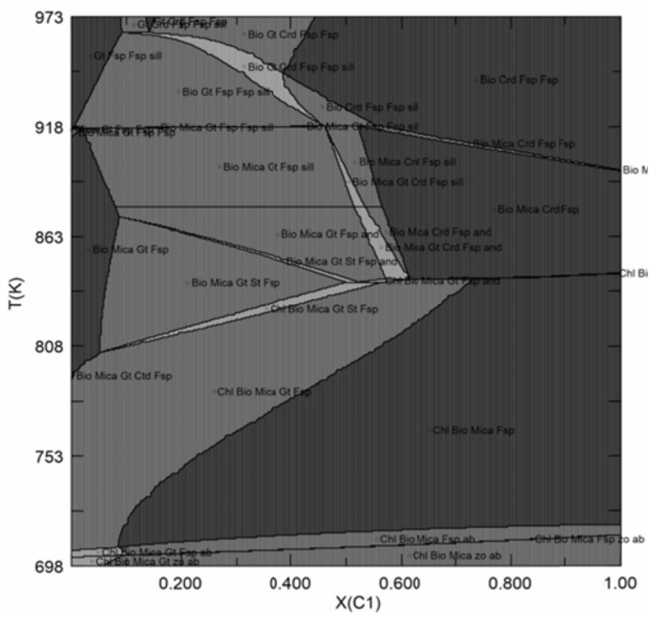
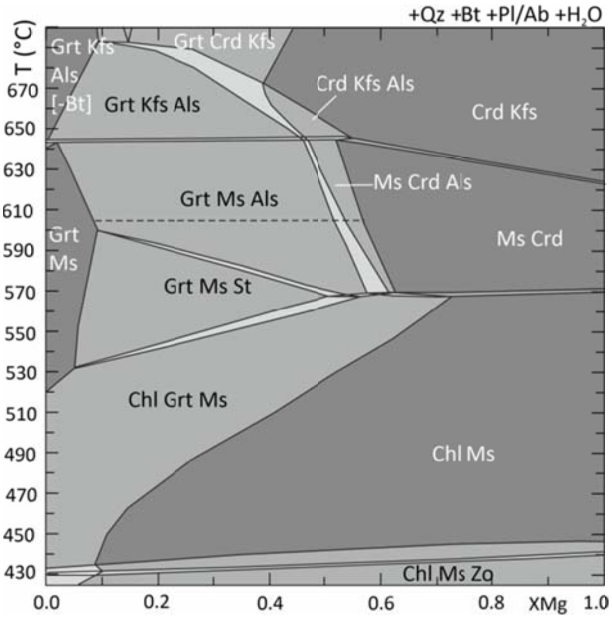
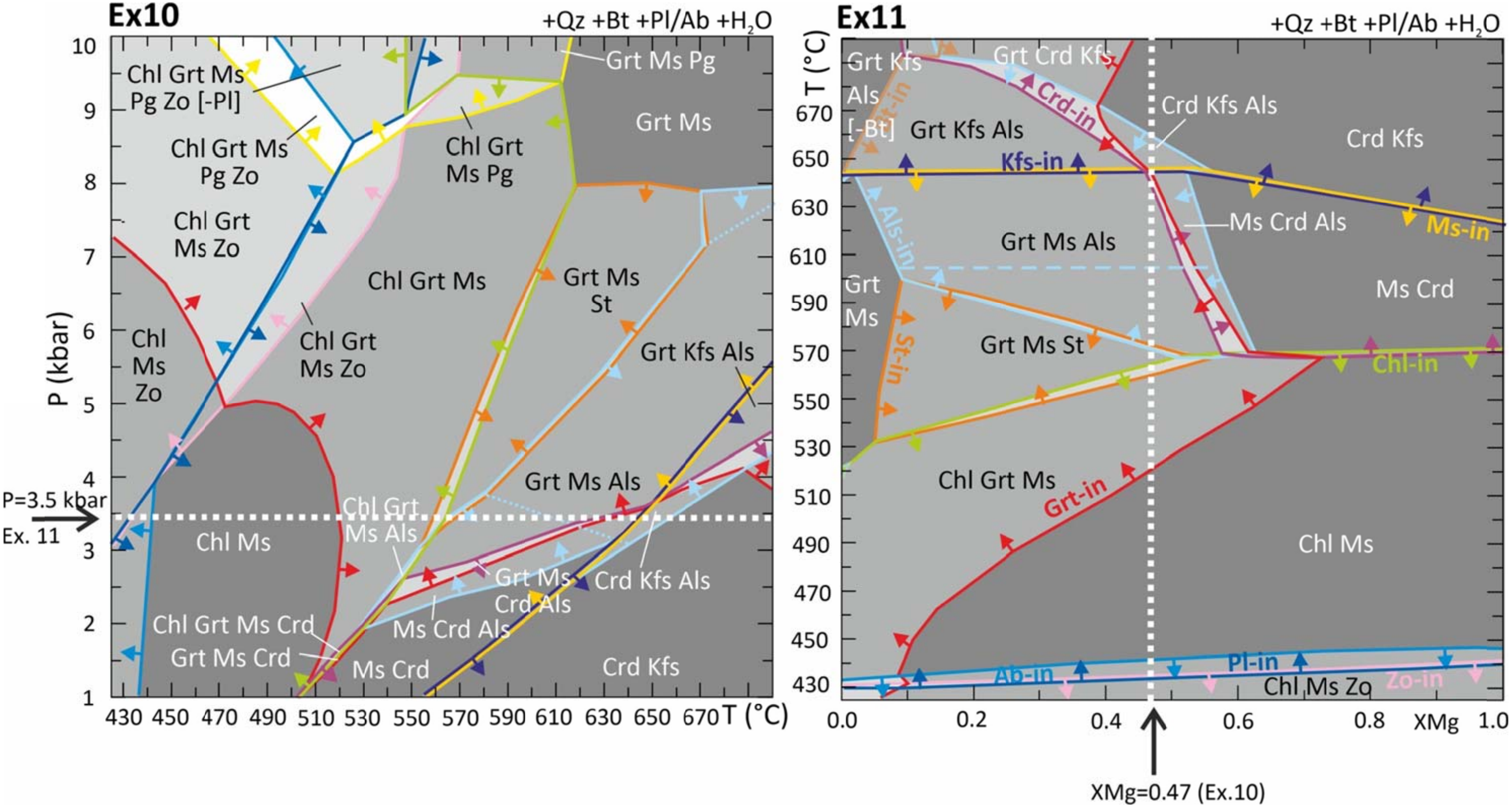

```
                    0.00     [0.0]  rotation (deg)
   plot_aspect_ratio     1.000      [1.0] x_axis_length/y_axis_length
   splines             T        [T] F
   tenth_ticks          F        [F] T
   text_scale          1.000     [1.] (rel)
   plot_extra_data       F         [T] F, to plot, e.g., experimental observations
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   3 fields for: Bio Mica Gt Fsp Fsp sill
There are   3 fields for: Chl Bio Mica Gt St Fsp
There are  11 fields for: Bio Mica Gt St Fsp and
There are  17 fields for: Chl Bio Mica Fsp zo ab
There are   3 fields for: Bio Mica Gt Crd Fsp sill
There are   2 fields for: Bio Mica Crd Fsp and
There are   2 fields for: Bio Mica Crd Fsp Fsp
There are   5 fields for: Chl Bio Mica Crd Fsp
There are   2 fields for: Chl Bio Mica Gt Ctd Fsp
```







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 – P-T pseudosection for a “real” METAPELITE and ISOPLETHS THERMOBAROMETRY

In this exercise, a P-T pseudosection is modelled for a “real” metapelite, with the aim of retrieving the equilibrium P-T conditions of a specific metamorphic stage.

The exercise illustrates how, once that the isochemical phase diagram is modelled, equilibrium P–T conditions can be constrained by comparing the predicted mineral assemblages and compositions with the observed ones. A first constraint is given by the modelled field which matches the observed mineral assemblage; however, this preliminary information should be refined (and cross-checked) by locating the modelled compositional isopleths correspondent to the measured mineral compositions. If the observed mineral assemblage and composition reflect equilibrium conditions, the modelled isopleths should intersect (or converge) in a single, narrow, P–T domain. The method is called “isopleth thermobarometry”.

To enhance the interpretation of isopleth thermobarometry, IntersecT (i.e., a Python package recently developed, see below) is further applied, which quantifies the quality of fit between the modelled and the observed composition of the phases and accounts for uncertainties in the measured mineral compositions.

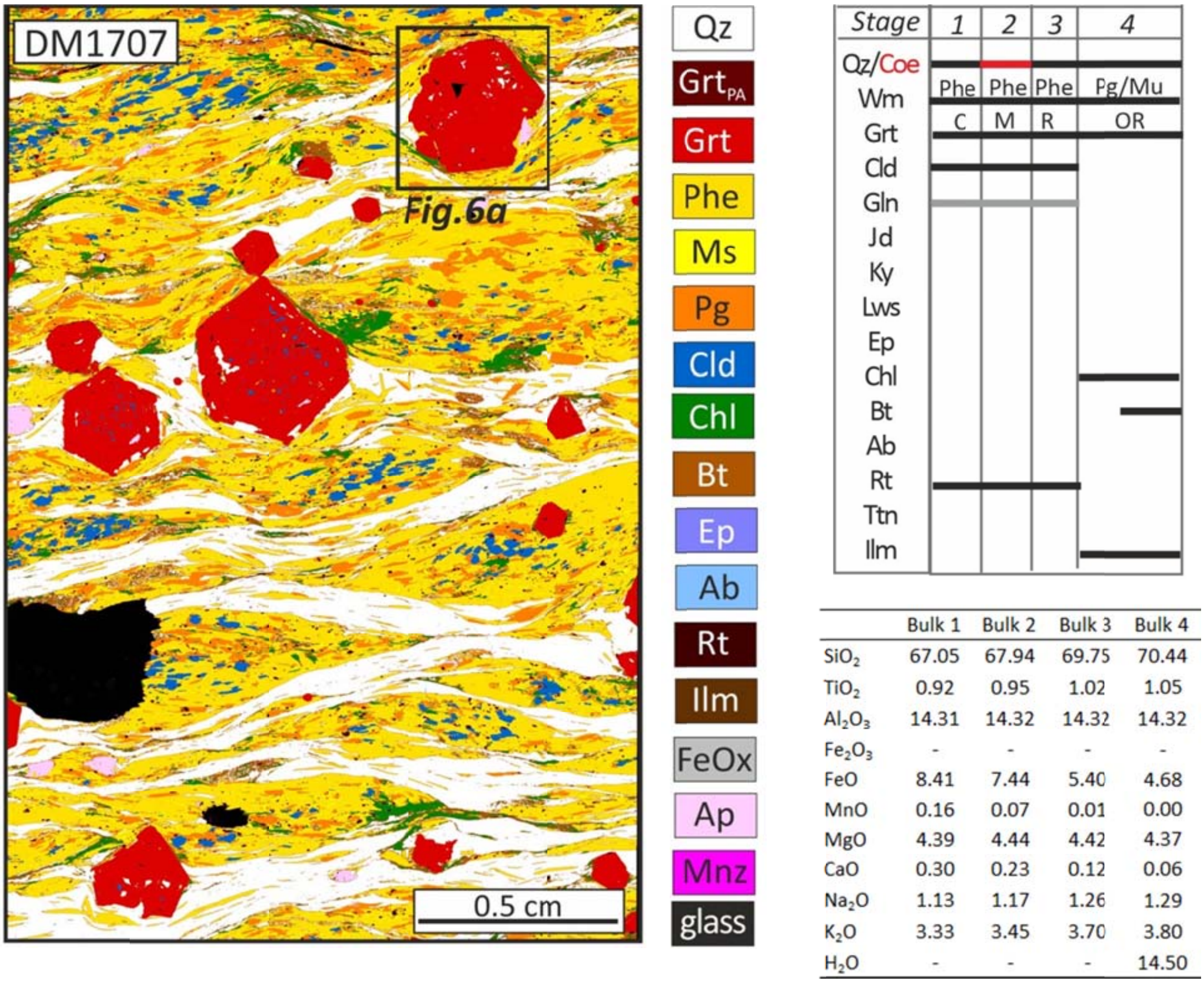
This exercise is based on the paper by Groppo et al. (2025) [Journal of Metamorphic Geology, 43, 359-383]. The modelled sample is DM1707 and the modelled metamorphic stage is Stage 2, i.e., growth of garnet mantle, which includes pseudomorphs after former coesite (see description below).

Petrography and mineral chemistry of sample DM1707

This sample consists of quartz, phengite/muscovite, paragonite, garnet, chloritoid, minor chlorite and biotite and accessory rutile, ilmenite and apatite. Large idioblastic garnet porphyroblasts, up to 5 mm in diameter, are mostly pre-kinematic with respect to the main foliation (S_m), except for their outermost rims, ca. 50 µm thick, which appears in equilibrium with S_m. Garnet shows a strong prograde zoning, with Sps decreasing and Prp increasing from core (GrtC) to rim (GrtR), except for the outermost rim (GrtOR) where Prp drops down. The Grs+Adr components show a different behaviour, decreasing from GrtC toward garnet mantle (GrtM) and then increasing from GrtR to GrtOR. Average compositions of each garnet domain are as follows: GrtC: Alm$_{78}$Sps$_{9}$Prp$_{7}$Grs+Adr$_{6}$, **GrtM: Alm$_{81}$Sps$_{4}$Prp$_{10}$Grs+Adr$_{5}$**, GrtR: Alm$_{79}$Sps$_{1}$Prp$_{14}$Grs+Adr$_{6}$, GrtOR: Alm$_{81}$Sps$_{0}$Prp$_{9}$Grs+Adr$_{10}$. GrtC and GrtM mostly include quartz, chloritoid, glaucophane (pseudomorphically replaced by fine-grained muscovite and paragonite) and rutile, whereas GrtR and GrtOR are free of inclusions. Chloritoid inclusions have different compositions in different garnet domains: chloritoid included in GrtC is Fe-richer (Cld in GrtC: XMg=0.16-0.17) than that included in GrtM and GrtR (**Cld in GrtM: XMg=0.17-0.20**; Cld in GrtR: XMg=0.20-0.21). **Polycrystalline inclusions of quartz, ranging in size from 50 µm to 400 µm, and surrounded by radial cracks, locally occur in GrtM, and are interpreted as pseudomorphs after former coesite**.

In the matrix, chloritoid occurs as mm-sized blasts aligned with the S_m; it is slightly zoned, with XMg increasing toward the rim (**CldC: XMg=0.22-0.28;** CldR: XMg=0.26-0.29). **Phengite defines the S_m; it is zoned, with Si contents varying from 3.52 a.p.f.u. in the core** to 3.34 a.p.f.u. in the rim. Prismatic to lozenge-shaped pseudomorphs after mm-sized **glaucophane** are quite abundant and are aligned with the

S_m; they consist of a fine-grained aggregate of muscovite (Si=3.09-3.18 a.p.f.u.), biotite, chlorite and quartz. Paragonite and chlorite are post-kinematic, forming large flakes that statically overgrow the S_m.



	Bulk 1	Bulk 2	Bulk 3	Bulk 4
SiO_2	67.05	67.94	69.75	70.44
TiO_2	0.92	0.95	1.02	1.05
Al_2O_3	14.31	14.32	14.32	14.32
Fe_2O_3	-	-	-	-
FeO	8.41	7.44	5.40	4.68
MnO	0.16	0.07	0.01	0.00
MgO	4.39	4.44	4.42	4.37
CaO	0.30	0.23	0.12	0.06
Na_2O	1.13	1.17	1.26	1.29
K_2O	3.33	3.45	3.70	3.80
H_2O	-	-	-	14.50

Input data

- The P-T pseudosections is calculated in the **MnNKCFMASTH system** using the data set from Holland & Powell (2011) **(ds6.2)**.
- The following **solution models** are used: garnet, white mica, biotite, chlorite, chloritoid, staurolite (White et al., 2014), omphacite and clino-amphibole (Green et al., 2007, 2016), epidote (Holland & Powell, 2011), carpholite (Smye et al., 2010), ilmenite (White et al., 2000, 2014), and feldspar (Fuhrman & Lindsley, 1988).
- Fractionation effects on the bulk composition due to the growth of zoned garnet porphyroblasts are considered by calculating different phase assemblage diagrams, each one used to model the P-T conditions for the growth of different garnet domains: (i) GrtC (Bulk 1 = MBC, Measured Bulk Composition), (ii) **GrtM (Bulk 2 = MBC – GrtC)**, (iii) GrtR (Bulk 3 = MBC – GrtC – GrtM), and (iv) GrtOR (Bulk 4 = MBC – GrtC – GrtM – GrtR).
- **Fluid saturation (pure H_2O**, EoS of Holland & Powell, 1998) is assumed to model the prograde stages of garnet growth (i.e. GrtC, GrtM and GrtR).

(1) Definition of the problem (BUILD)

Bulk composition (mol%): **SiO2=67.94; TiO2=0.95; Al2O3=14.32, FeO=7.44, MnO=0.07, MgO=4.44, CaO=0.23, Na2O=1.17, K2O=3.45**

T=723-873°C

P=15-35 kbar

Because the problem is similar to that of Ex. 10, we can skip the BUILD session and directly edit the input file, starting from that of Ex. 10.

Add SiO2, MnO and TiO2 in the list of thermodynamic components; delete SiO2 from the list of saturated components;

```
begin thermodynamic component list
Na2O   1  1.17000      0.00000      0.00000     molar amount
MgO    1  4.44000      0.00000      0.00000     molar amount
Al2O3  1  14.3200      0.00000      0.00000     molar amount
SiO2   1  67.9400      0.00000      0.00000     molar amount
K2O    1  3.45000      0.00000      0.00000     molar amount
CaO    1  0.23000      0.00000      0.00000     molar amount
TiO2   1  0.95000      0.00000      0.00000     molar amount
MnO    1  0.07000      0.00000      0.00000     molar amount
FeO    1  7.44000      0.00000      0.00000     molar amount
end thermodynamic component list

begin saturated component list
end saturated component list
```

Add the carpholite, clino-amphibole, omphacite and ilmenite solution models.

```
begin solution phase list
Chl(W)
Bi(W)
Mica(W)
Gt(W)
Ctd(W)
St(W)
Crd(W)
feldspar
Carp(SGH)
cAmph(G)
Omph(GHP)
Ilm(WPH)
end solution phase list
```

Change the P-T range of interest

```
35000.00   873.000   0.00000  0.00000   0.00000    max p, t, xco2, mu_1, mu_2
15000.00   723.000   0.00000  0.00000   0.00000    min p, t, xco2, mu_1, mu_2
0.00000   0.00000   0.00000  0.00000    0.00000    unused place holder post 06
```

(2) Doing the calculation (VERTEX)

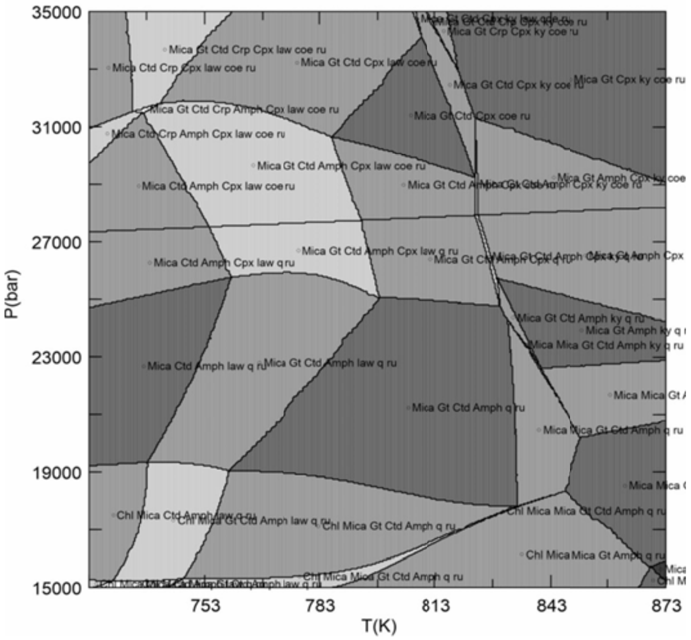
Run VERTEX to make the calculation:

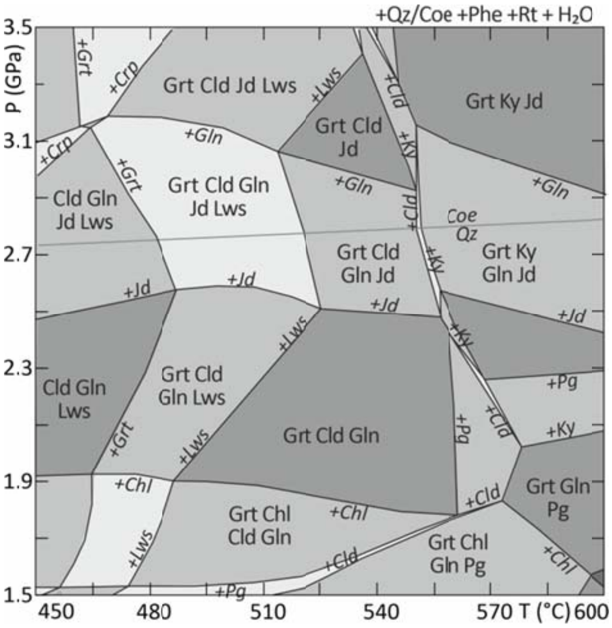
```
C:\PERPLEX\Perplex7110>vertex

Perple_X release 7.1.10 Dec 21, 2024.
Copyright (C) 1986-2024 James A D Connolly <www.perplex.ethz.ch/copyright.html>.

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

(3) Plotting the calculated phase diagram (PSSECT)

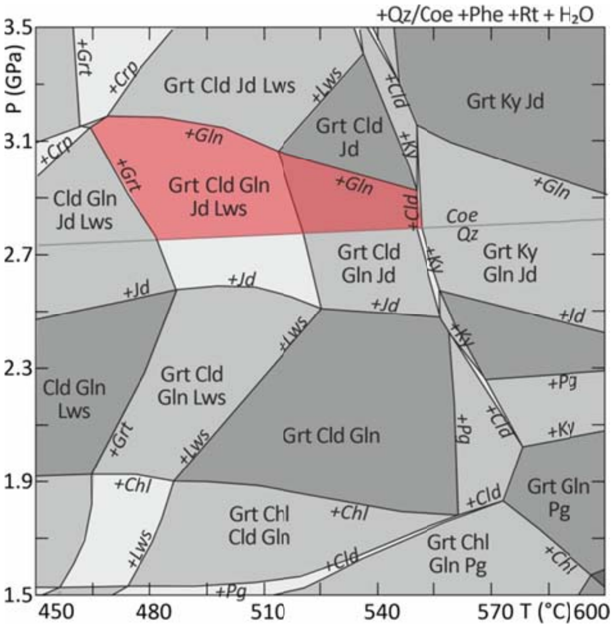
Run PSSECT to plot the calculated pseudosection:

```
C:\PERPLEX\Perplex7110>pssect

Perple_X release 7.1.10 Dec 21, 2024.
Copyright (C) 1986-2024 James A D Connolly <www.perplex.ethz.ch/copyright.html>.

Enter the project name (the name assigned in BUILD) [default = my_project]:
ex12

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)
   contour_t_interval       50.00    >0 [50.0]
   contour_p_interval     1000.00    >0 [1000.0]
   field_fill            T          [T] F
   field_label           T          [T] F
   numeric_field_label    F          [F] T, if T PSSECT writes list to *_assemblages.txt
   replicate_label       0.250      0->1 [0.025]
   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
   splines               T          [T] F
   tenth_ticks           F          [F] T
   text_scale            1.000      [1.] (rel)
   plot_extra_data       F          [T] F, to plot, e.g., experimental observations
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
```





Pseudosection topology - Among the Al-rich phases, chlorite is stable at P<1.9 GPa, whereas garnet is stable over a large P-T interval; the stability of chloritoid and kyanite is temperature dependent, with the first predicted at T<540-570 °C and the second at T>540-570 °C. Paragonite, glaucophane and jadeite are the Na-bearing phases stable at low, medium and high pressure, respectively. Ca is mostly stored in lawsonite at low temperatures, and in garnet at higher temperatures; however, given the very low amount of CaO in the bulk composition, the predicted mode of lawsonite is always negligible (i.e. <1 vol%).



A first constraint on the equilibrium P–T conditions for stage 2 is given by the modelled field(s) which match(es) the observed mineral assemblage. **The two red fields show the best fit between the observed (i.e., Coe + Phe + GrtM + Cld + Gln + Rt) and the modelled (i.e., Coe + Phe + GrtM + Cld + Gln + Jd ± Lws + Rt) phase assemblages**. The predicted amounts of lawsonite and jadeite are negligible in both fields (i.e., Lws <1vol%, Jd<3vol%).

(4) Calculating compositional isopleths for Grt, Cld and Phe (WERAMI)

To further constrain the P-T conditions of stage 2, isopleth thermobarometry is applied. The compositional isopleths modelled for garnet, chloritoid and phengite and correspondent to the measured mineral compositions should converge in a single, narrow, P–T domain.

Run WERAMI to calculate compositional isopleths for garnet (Sps, Prp and Grs), chloritoid (XMg=MgO/(MgO+FeO)) and phengite (Si a.p.f.u.).

```
C:\PERPLEX\Perplex7110>werami

Perple_X release 7.1.10 Dec 21, 2024.
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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
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] 0-150
    aq_solvent_composition  y        [y] m: y => mol fraction, m => molality
    aq_solute_composition   m        y [m]: y => mol fraction, m => molality
    spreadsheet             T        [T] F
    logarithmic_p           F        [F] T
    logarithmic_X           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           T        [T] F
    solution_names          abb      [model] abbreviation full
    structural_formulae     T        [T] F
    output_species          T        [T] F
    output_species_props    F        [F] T
    seismic_output          som      [some] none all
    poisson_test            F        [F] T
    interim_results         aut      [auto] off manual
    sample_on_grid          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
    finite_strain_alpha     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      [2] >0
  finite_difference_p    1.0E+04  [1d4] >0; fraction = 1.0E-03   [1d-3]
 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
  fluid_shear_modulus    T        [T] F
  phi_d                  0.36     [0.36] 0->1
 Error/warning control options:
  pause_on_error         T        [T] F
  max_warn_limit         5        [5]
  warn_interactive       T        [T] F
  aq_error_ver100        F        [F] T, abort during iteration
  aq_error_ver101        T        [T] F, solute undersaturation abort
  aq_error_ver102        T        [T] F, pure + impure solvent abort
  aq_error_ver103        T        [T] F, out-of-range HKF g abort
  aq_error_ver104        T        [T] F, abort on failed respeciation
  warning_ver637         T        [T] F
  error_ver109           T        [T] F
  do_not_reset_options   F        [F] T, prevents automatic resets
To change these options see: www.perplex.ethz.ch/perplex_options.html
------------------------------------------------------------------------------
Select operational mode:
   1 - properties at specified conditions
   2 - properties on a 2d grid
   3 - properties along a 1d path
   4 - as in 3, but input from file
   0 - EXIT
2

Select a property:
  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.
Units (mass or molar) are controlled by the composition keyword in perplex_option.dat.
```

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

```
y

Compositions are defined as a ratio of the form:
    Sum {w(i)*y(i), i = 1, c1} / Sum {w(i)*y(i), i = c2, c3}
            y(j)   = mole fraction of  species  j
            w(j)   = weighting factor of  species  j (usually 1)
How many  species  in the numerator of the composition (<15)?
```

We want to calculate the Sps isopleths, this means that we have one component in the numerator (spss) and zero components in the denominator

```
1

Enter  species  indices and weighting factors for the numerator:
  1 - spss
  2 - alm
```

```
   3 - py
   4 - gr
1
1

How many  species  in the denominator of the composition (<14)?
Enter zero to use the numerator as a composition.
0

The compositional variable is: 1.0 spss

Change it (y/n)?
n

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

Select an additional property or enter 0 to finish:
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.
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)*y(i), i = 1, c1} / Sum {w(i)*y(i), i = c2, c3}
               y(j)   = mole fraction of  species  j
               w(j)   = weighting factor of  species  j (usually 1)
How many  species  in the numerator of the composition (<15)?
1

Enter  species  indices and weighting factors for the numerator:
   1 - spss
   2 - alm
   3 - py
   4 - gr
3
1

How many  species  in the denominator of the composition (<14)?
Enter zero to use the numerator as a composition.
0

The compositional variable is: 1.0 py

Change it (y/n)?
n

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

```
Select an additional property or enter 0 to finish:
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.
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)*y(i), i = 1, c1} / Sum {w(i)*y(i), i = c2, c3}
         y(j)   = mole fraction of  species  j
         w(j)   = weighting factor of  species  j (usually 1)

How many  species  in the numerator of the composition (<15)?
1

Enter  species  indices and weighting factors for the numerator:
  1 - spss
  2 - alm
  3 - py
  4 - gr
4
1

How many  species  in the denominator of the composition (<14)?
Enter zero to use the numerator as a composition.
0

The compositional variable is: 1.0 gr

Change it (y/n)?
n

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

Select an additional property or enter 0 to finish:
8

Enter solution (left justified):
Ctd(W)

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

Now we want to calculate the ratio Mg/(Mg+Fe) in Cld, so we should answer NO to define the composition in terms of the systems components (i.e., MgO, FeO). We will have one component in the numerator (MgO) and two components in the denominator (MgO + FeO).

```
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 (<15)?
1

Enter component indices and weighting factors for the numerator:
  1 - Na2O
  2 - MgO
  3 - Al2O3
  4 - SiO2
  5 - K2O
  6 - CaO
  7 - TiO2
  8 - MnO
  9 - FeO
 10 - H2O
2
1

How many components in the denominator of the composition (<14)?
Enter zero to use the numerator as a composition.
2

Enter component indices and weighting factors for the denominator:
  1 - Na2O
  2 - MgO
  3 - Al2O3
  4 - SiO2
  5 - K2O
  6 - CaO
  7 - TiO2
  8 - MnO
  9 - FeO
 10 - H2O
2
1
9
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)4]

Select an additional property or enter 0 to finish:
8

Enter solution (left justified):
Mica(W)

Define the composition in terms of the species/endmembers of Mica(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.
```

Now we want to calculate the Si a.p.f.u. in Phe, so we should answer NO to define the composition in terms of the systems components (i.e. SiO2). We will have one component in the numerator (SiO2) and no components in the denominator.

```
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 (<15)?
1

Enter component indices and weighting factors for the numerator:
  1 - Na2O
  2 - MgO
  3 - Al2O3
  4 - SiO2
  5 - K2O
  6 - CaO
  7 - TiO2
  8 - MnO
  9 - FeO
 10 - H2O
4
1

How many components in the denominator of the composition (<14)?
Enter zero to use the numerator as a composition.
0

The compositional variable is: 1.0 SiO2

Change it (y/n)?
n

This composition will be designated: C[Mica(W)5]

Select an additional property or enter 0 to finish:
0
```

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

**warning ver178** at T(K)=   723.0     P(bar)=  0.1500E+05
the shear modulus of: Chl
is missing or invalid and has been estimated with the poisson_ratio option
…

2 immiscible phases of Mica(W)
coexist with the following molar  compositions:
   Na2O    MgO     Al2O3   SiO2    K2O     CaO     TiO2    MnO     FeO     H2O
    0.500   0.000   1.500   3.000   0.000   0.000   0.000   0.000   0.000   1.000
    0.041   0.129   1.253   3.247   0.459   0.001   0.000   0.000   0.119   1.000

Current conditions:
    T(K)     =   723.0000
    P(bar)   =   15000.00
    Y(CO2)   =   0.000000

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.
```

Phe and Pg have been modelled using the same solid solution model Mica(W); therefore, in the modelled pseudosection, you have fields in which two micas coexist. For those fields where there are two stable micas, you should specify what do you want to calculate (i.e. isopleths for Phe or for Pg?).

You should choose one of the above criteria: in this case, we want to calculate the isopleths for the K-white mica, therefore we can specify that the phase of interest should be identified based on the maximum K2O 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.
```

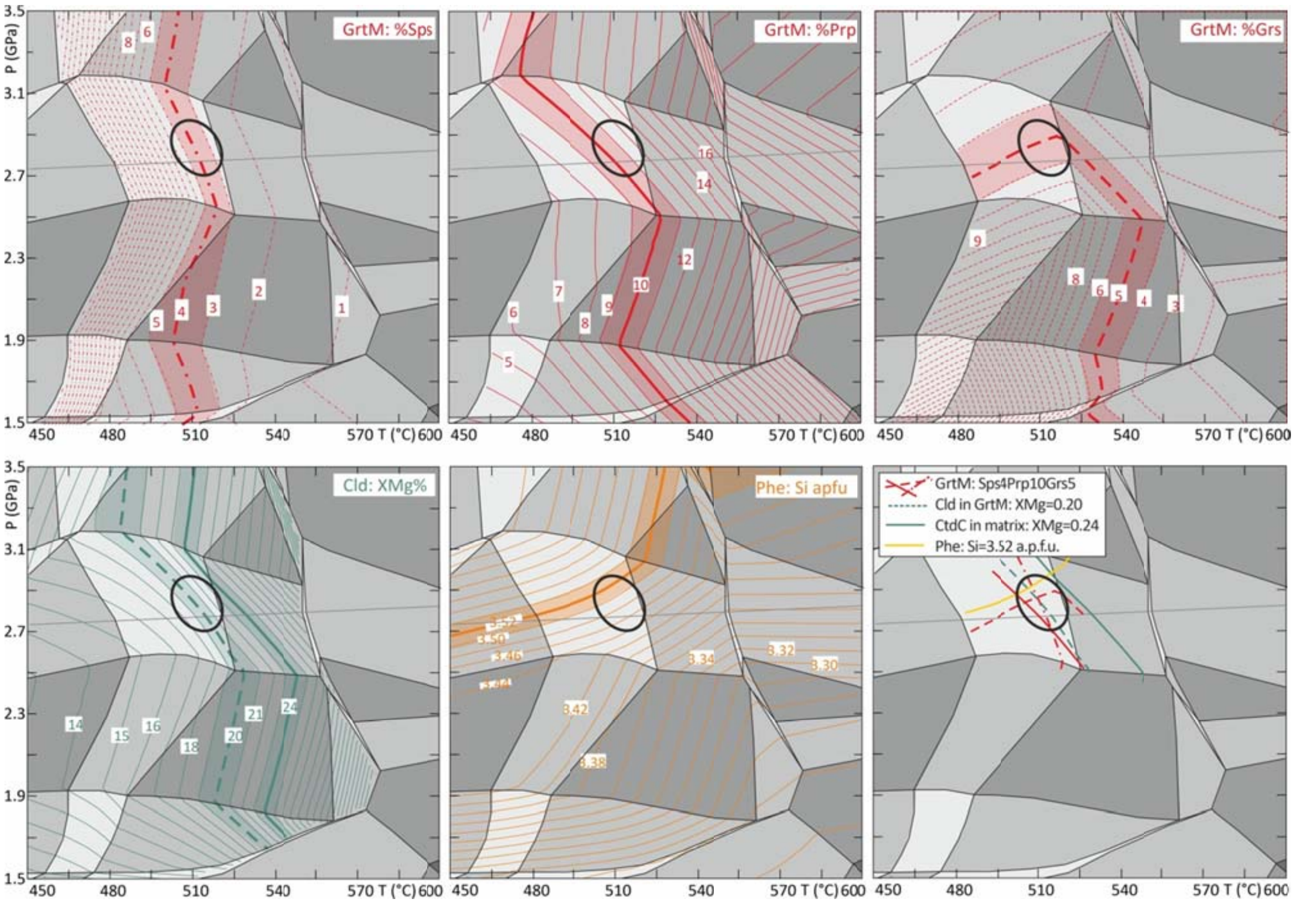
Read carefully this note.

```
Define the composition in terms of the species/endmembers of Mica(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 (<15)?
1

Enter component indices and weighting factors for the numerator:
   1 - Na2O
   2 - MgO
   3 - Al2O3
   4 - SiO2
   5 - K2O
   6 - CaO
   7 - TiO2
   8 - MnO
   9 - FeO
  10 - H2O
5
2

How many components in the denominator of the composition (<14)?
Enter zero to use the numerator as a composition.
0

The compositional variable is: 2.0 K2O

Change it (y/n)?
N

Data ranges excluding values equal to bad_number (       NaN) specified in perplex_option.dat:
     C[Gt(W)1]      C[Gt(W)2]      C[Gt(W)3]      C[Ctd(W)4]     C[Mica(W)5]
min   0.762821E-002  0.275148E-001  0.158087E-001  0.891702E-001   3.18427
max   0.219305       0.251029       0.312440       0.410540        3.67303
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
```

(5) Qualitative isopleth thermobarometry (PYWERAMI)

Use PYWERAMI to plot the calculated compositional isopleths.



Stage 2 equilibration is recorded at 500-515 °C, 2.7-3.0 GPa, within the Qz/Coe + Phe + Grt + Cld + Gln + Jd (+ Lws) + Rt + H_2O assemblage field, using compositions of GrtM (Alm$_{81}$Sps$_4$Prp$_{10}$Grs$_5$), chloritoid (Cld in GrtM: XMg=0.20; CldC in matrix: XMg=0.24) and phengite (Si=3.52 a.p.f.u.). The modelled assemblage is consistent with that observed; notably, GrtM is predicted to grow close to the quartz-coesite transition, consistently with the occurrence of coesite pseudomorphs in that garnet domain.

This approach constrains the fit of the isopleths in a QUALITATIVE way. In the following, the quality of fit between the modelled and the observed composition of the phases will be QUANTITATIVELY assessed using IntersecT**,** a newly developed Python package, which considers the uncertainty related to the measured compositions and assesses the weight of the considered phases through reduced $\chi 2$ statistics.

(6) Quantitative isopleth thermobarometry (PYWERAMI + INTERSECT)

IntersecT is an open-source Python package that allows quantitative isopleth thermobarometry on Perple_X P-T-X phase diagrams. IntersecT uses the quality factor approach for compositions as first implemented in Bingo-Antidote (Q_{cmp}; Duesterhoeft and Lanari, 2020), which quantitatively assesses the quality of fit between the modelled and the observed composition of the phases, involving uncertainty related to the measured compositions. A reduced χ2 statistic is applied to assess the weight of the considered phases. This allows for the down-weighting of outlier data, whether due to model problems or incorrect assumptions. IntersecT thus enhances the interpretation of isopleth thermobarometry applied to Perple_X results, by accounting for uncertainties in the measured mineral compositions.

IntersecT is available at https://github.com/neoscalc/IntersecT and presented in Nerone et al. (2025), Computers & Geosciences, https://doi.org/10.1016/j.cageo.2025.105949

The WERAMI output file must contain only the phases considered in equilibrium, and their composition must be in a.p.f.u. to allow the propagation of uncertainties. To properly calculate the Q_{cmp}, the extracted properties should include the a.p.f.u. of the elements involved in substitutions in the solution models of each phase. Because the recognition of the equilibrium assemblage is the first discriminant, in the case of index minerals that only show a few substitutions (e.g., chloritoid in this example), these should be added to the input data. Similarly, for the occurrence of index minerals that do not display substitutions (e.g., coesite in this example), we propose adding a compositional parameter to the input data even if it is constant, e.g., using the routine number 36 of WERAMI. This will allow IntersecT to mask out the phase fields where this phase is not stable.

Input files

(1) WERAMI .tab file

Using the WERAMI routine of Perple_X, export the a.p.f.u. of the elements for each phase that are considered at equilibrium. Columns can be added or deleted manually (e.g., using Excel), but do not modify the rows.

Run WERAMI, property 8 (Composition - Mol, Mass, or Wt% - of a solution phase), to calculate the following compositional variables:

- Mg, Ca, Mn, Fe (a.p.f.u.) in garnet
- Mg, Fe (a.p.f.u.) in chloritoid
- Mg, Fe, Si, Al (a.p.f.u.) in phengite

Then, run again WERAMI, property 36 (All phase &/or system properties), to calculate the following compositional variables:

- Si (a.p.f.u.) in coesite

```
C:\PERPLEX\Perplex7110>werami

Perple_X release 7.1.10 Dec 21, 2024.
Copyright (C) 1986-2024 James A D Connolly <www.perplex.ethz.ch/copyright.html>.

Enter the project name (the name assigned in BUILD) [default = my_project]:
ex12

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] 0-150
   aq_solvent_composition  y       [y] m: y => mol fraction, m => molality
   aq_solute_composition   m       y [m]: y => mol fraction, m => molality
   spreadsheet            T       [T] F
   logarithmic_p          F       [F] T
   logarithmic_X          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          T       [T] F
   solution_names         abb     [model] abbreviation full
   structural_formulae    T       [T] F
   output_species         T       [T] F
   output_species_props   F       [F] T
   seismic_output         som     [some] none all
   poisson_test           F       [F] T
   interim_results        aut     [auto] off manual
   sample_on_grid         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
   finite_strain_alpha    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     [2] >0
   finite_difference_p    1.0E+04  [1d4] >0; fraction = 1.0E-03   [1d-3]
 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
   fluid_shear_modulus    T       [T] F
   phi_d                  0.36     [0.36] 0->1
  Error/warning control options:
   pause_on_error         T       [T] F
   max_warn_limit          5      [5]
   warn_interactive       T       [T] F
   aq_error_ver100        F       [F] T, abort during iteration
   aq_error_ver101        T       [T] F, solute undersaturation abort
   aq_error_ver102        T       [T] F, pure + impure solvent abort
   aq_error_ver103        T       [T] F, out-of-range HKF g abort
   aq_error_ver104        T       [T] F, abort on failed respeciation
   warning_ver637         T       [T] F
   error_ver109           T       [T] F
   do_not_reset_options   F       [F] T, prevents automatic resets
To change these options see: www.perplex.ethz.ch/perplex_options.html
--------------------------------------------------------------------------------

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

Select a property:
   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.
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 (<15)?
1

Enter component indices and weighting factors for the numerator:
  1 - Na2O
  2 - MgO
  3 - Al2O3
  4 - SiO2
  5 - K2O
  6 - CaO
  7 - TiO2
  8 - MnO
  9 - FeO
```

```
 10 - H2O
2
1

How many components in the denominator of the composition (<14)?
Enter zero to use the numerator as a composition.
0

The compositional variable is: 1.0 MgO

Change it (y/n)?
n

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

Select an additional property or enter 0 to finish:
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.
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 (<15)?
1

Enter component indices and weighting factors for the numerator:
  1 - Na2O
  2 - MgO
  3 - Al2O3
  4 - SiO2
  5 - K2O
  6 - CaO
  7 - TiO2
  8 - MnO
  9 - FeO
 10 - H2O
6
1

How many components in the denominator of the composition (<14)?
Enter zero to use the numerator as a composition.
0
```

```
The compositional variable is: 1.0 CaO
Change it (y/n)?
n

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

Select an additional property or enter 0 to finish:
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.
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 (<15)?
1

Enter component indices and weighting factors for the numerator:
   1 - Na2O
   2 - MgO
   3 - Al2O3
   4 - SiO2
   5 - K2O
   6 - CaO
   7 - TiO2
   8 - MnO
   9 - FeO
  10 - H2O
8
1

How many components in the denominator of the composition (<14)?
Enter zero to use the numerator as a composition.
0

The compositional variable is: 1.0 MnO

Change it (y/n)?
n

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

Select an additional property or enter 0 to finish:
```

```
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.
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 (<15)?
1

Enter component indices and weighting factors for the numerator:
  1 - Na2O
  2 - MgO
  3 - Al2O3
  4 - SiO2
  5 - K2O
  6 - CaO
  7 - TiO2
  8 - MnO
  9 - FeO
 10 - H2O
9
1

How many components in the denominator of the composition (<14)?
Enter zero to use the numerator as a composition.
0

The compositional variable is: 1.0 FeO

Change it (y/n)?
n

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

Select an additional property or enter 0 to finish:
8

Enter solution (left justified):
Ctd(W)

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

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

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

Compositions are defined as a ratio of the form:
    Sum {w(i)*n(i), i = 1, c1} / Sum {w(i)*n(i), i = c2, c3}
            n(j)   = molar amount  of component j
            w(j)   = weighting factor of component j (usually 1)
How many components in the numerator of the composition (<15)?
1

Enter component indices and weighting factors for the numerator:
  1 - Na2O
  2 - MgO
  3 - Al2O3
  4 - SiO2
  5 - K2O
  6 - CaO
  7 - TiO2
  8 - MnO
  9 - FeO
 10 - H2O
2
1

How many components in the denominator of the composition (<14)?
Enter zero to use the numerator as a composition.
0

The compositional variable is: 1.0 MgO

Change it (y/n)?
n

This composition will be designated: C[Ctd(W)5]

Select an additional property or enter 0 to finish:
8

Enter solution (left justified):
Ctd(W)

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

Answer no to define a composition in terms of the systems components.
Units (mass or molar) are controlled by the composition keyword in perplex_option.dat.
n

Compositions are defined as a ratio of the form:
    Sum {w(i)*n(i), i = 1, c1} / Sum {w(i)*n(i), i = c2, c3}
            n(j)   = molar amount  of component j
            w(j)   = weighting factor of component j (usually 1)
```

```
How many components in the numerator of the composition (<15)?
1

Enter component indices and weighting factors for the numerator:
   1 - Na2O
   2 - MgO
   3 - Al2O3
   4 - SiO2
   5 - K2O
   6 - CaO
   7 - TiO2
   8 - MnO
   9 - FeO
  10 - H2O
9
1

How many components in the denominator of the composition (<14)?
Enter zero to use the numerator as a composition.
0

The compositional variable is: 1.0 FeO

Change it (y/n)?
n

This composition will be designated: C[Ctd(W)6]

Select an additional property or enter 0 to finish:
8

Enter solution (left justified):
Mica(W)

Define the composition in terms of the species/endmembers of Mica(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 (<15)?
1

Enter component indices and weighting factors for the numerator:
   1 - Na2O
   2 - MgO
   3 - Al2O3
```

```
   4 - SiO2
   5 - K2O
   6 - CaO
   7 - TiO2
   8 - MnO
   9 - FeO
  10 - H2O
2
1

How many components in the denominator of the composition (<14)?
Enter zero to use the numerator as a composition.
0

The compositional variable is: 1.0 MgO

Change it (y/n)?
n

This composition will be designated: C[Mica(W)7]

Select an additional property or enter 0 to finish:
8

Enter solution (left justified):
Mica(W)

Define the composition in terms of the species/endmembers of Mica(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 (<15)?
1

Enter component indices and weighting factors for the numerator:
   1 - Na2O
   2 - MgO
   3 - Al2O3
   4 - SiO2
   5 - K2O
   6 - CaO
   7 - TiO2
   8 - MnO
   9 - FeO
```

```
 10 - H2O
9
1

How many components in the denominator of the composition (<14)?
Enter zero to use the numerator as a composition.
0

The compositional variable is: 1.0 FeO

Change it (y/n)?
n

This composition will be designated: C[Mica(W)8]

Select an additional property or enter 0 to finish:
8

Enter solution (left justified):
Mica(W)

Define the composition in terms of the species/endmembers of Mica(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 (<15)?
1

Enter component indices and weighting factors for the numerator:
  1 - Na2O
  2 - MgO
  3 - Al2O3
  4 - SiO2
  5 - K2O
  6 - CaO
  7 - TiO2
  8 - MnO
  9 - FeO
 10 - H2O
4
1

How many components in the denominator of the composition (<14)?
Enter zero to use the numerator as a composition.
0
```

```
The compositional variable is: 1.0 SiO2

Change it (y/n)?
n

This composition will be designated: C[Mica(W)9]

Select an additional property or enter 0 to finish:
8

Enter solution (left justified):
Mica(W)

Define the composition in terms of the species/endmembers of Mica(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 (<15)?
1

Enter component indices and weighting factors for the numerator:
  1 - Na2O
  2 - MgO
  3 - Al2O3
  4 - SiO2
  5 - K2O
  6 - CaO
  7 - TiO2
  8 - MnO
  9 - FeO
 10 - H2O
3
2

How many components in the denominator of the composition (<14)?
Enter zero to use the numerator as a composition.
0

The compositional variable is: 2.0 Al2O3

Change it (y/n)?
n

This composition will be designated: C[Mica(W)10]
```

```
Select an additional property or 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 [default]
   2 -  119 x  119 nodes
   3 -  237 x  237 nodes
   4 -  473 x  473 nodes
1

**warning ver178** at T(K)=   723.0     P(bar)=  0.1500E+05
the shear modulus of: Chl
is missing or invalid and has been estimated with the poisson_ratio option
...

2 immiscible phases of Mica(W)
coexist with the following molar  compositions:
   Na2O    MgO     Al2O3   SiO2    K2O     CaO     TiO2    MnO     FeO     H2O
    0.500   0.000   1.500   3.000   0.000   0.000   0.000   0.000   0.000   1.000
    0.041   0.129   1.253   3.247   0.459   0.001   0.000   0.000   0.119   1.000

Current conditions:
    T(K)     =   723.0000
    P(bar)   =   15000.00
    Y(CO2)   =   0.000000

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.
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.

Define the composition in terms of the species/endmembers of Mica(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 (<15)?
1
```

```
Enter component indices and weighting factors for the numerator:
   1 - Na2O
   2 - MgO
   3 - Al2O3
   4 - SiO2
   5 - K2O
   6 - CaO
   7 - TiO2
   8 - MnO
   9 - FeO
  10 - H2O
5
2

How many components in the denominator of the composition (<14)?
Enter zero to use the numerator as a composition.
0

The compositional variable is: 2.0 K2O

Change it (y/n)?
N


Data ranges excluding values equal to bad_number (       NaN) specified in perplex_option.dat:
     C[Gt(W)1]      C[Gt(W)2]      C[Gt(W)3]      C[Gt(W)4]      C[Ctd(W)5]      C[Ctd(W)6]      C[Mica(W)7]      C[Mica(W)8]
C[Mica(W)9]    C[Mica(W)10]
min      0.825444E-001   0.474262E-001   0.228846E-001     1.49502          0.874914E-001   0.589081          0.103895
0.557448E-001   3.18427       1.65394
max    0.753086        0.937319        0.657914         2.51555        0.410277        0.896875        0.442826        0.248751
3.67303       2.63037
Output has been written to the 2d tab format file: ex12_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
```

```
C:\PERPLEX\Perplex7110>werami
Perple_X release 7.1.10 Dec 21, 2024.
Copyright (C) 1986-2024 James A D Connolly <www.perplex.ethz.ch/copyright.html>.

Enter the project name (the name assigned in BUILD) [default = my_project]:
ex12

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] 0-150
    aq_solvent_composition  y        [y] m: y => mol fraction, m => molality
    aq_solute_composition   m        y [m]: y => mol fraction, m => molality
    spreadsheet             T        [T] F
    logarithmic_p           F        [F] T
    logarithmic_X           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           T        [T] F
    solution_names          mod      [model] abbreviation full
    structural_formulae     T        [T] F
    output_species          T        [T] F
    output_species_props    F        [F] T
    seismic_output          som      [some] none all
    poisson_test            F        [F] T
    interim_results         aut      [auto] off manual
    sample_on_grid          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
    finite_strain_alpha     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      [2] >0
    finite_difference_p     1.0E+04  [1d4] >0; fraction = 1.0E-03   [1d-3]
  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
  fluid_shear_modulus    T        [T] F
  phi_d                  0.36     [0.36] 0->1
 Error/warning control options:
  pause_on_error         T        [T] F
  max_warn_limit         5        [5]
  warn_interactive       T        [T] F
  aq_error_ver100        F        [F] T, abort during iteration
  aq_error_ver101        T        [T] F, solute undersaturation abort
  aq_error_ver102        T        [T] F, pure + impure solvent abort
  aq_error_ver103        T        [T] F, out-of-range HKF g abort
  aq_error_ver104        T        [T] F, abort on failed respeciation
  warning_ver637         T        [T] F
  error_ver109           T        [T] F
  do_not_reset_options   F        [F] T, prevents automatic resets
To change these options see: www.perplex.ethz.ch/perplex_options.html
--------------------------------------------------------------------------------
Select operational mode:
    1 - properties at specified conditions
    2 - properties on a 2d grid
    3 - properties along a 1d path
    4 - as in 3, but input from file
    0 - EXIT
2

Select a property:
   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
36

In this mode you may tabulate:
   1 - properties of the system
   2 - properties of a phase
   3 - properties of the system and its phases
Output for option 1 & 2 can be plotted with PSPLOT, PYWERAMI or MatLab.
Output for option 3 can only be plotted with PHEMGP.

Select an option [default = 1]:
2

Enter solution or compound (left justified):
coe

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

**warning ver069** composition_phase is mole but composition_system is mass. As only one unit can be output for
property choice 36 system units will be indicated; the true units for phase compositions are mole

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 [default]
   2 -  119 x  119 nodes
   3 -  237 x  237 nodes
   4 -  473 x  473 nodes
1
```

Note that the resolution must be the same used to run Werami, property 8, for the other solution phases.

```
**warning ver178** at T(K)=   723.0     P(bar)=  0.1500E+05
the shear modulus of: Chl(W)
is missing or invalid and has been estimated with the poisson_ratio option
…

Data ranges excluding values equal to bad_number (       NaN) specified in perplex_option.dat:
    V,J/bar/mol     H,J/mol        Gruneisen_T     Ks,bar          Gs,bar          v0,km/s         vp,km/s         vs,km/s         vp/vs
rho,kg/m3       G,J/mol         cp,J/K/mol      alpha,1/K       beta,1/bar      S,J/K/mol       n,mol           N,g             Ks_{T},bar/K
Gs_{T},bar/K    Ks_{P}          Gs_P            v0_{T}          vp_{T}          vs_{T}          v0_{P}          vp_P            vs_{P}          cp/cv
vol,%           wt,%            mol,%           Na2O,wt%        MgO,wt%         Al2O3,wt%       SiO2,wt%        K2O,wt%         CaO,wt%
TiO2,wt%        MnO,wt%         FeO,wt%         H2O,wt%         mu[Na2O],J/mol  mu[MgO],J/mol   mu[Al2O3],J/mo
mu[SiO2],J/mol mu[K2O],J/mol  mu[CaO],J/mol  mu[TiO2],J/mol mu[MnO],J/mol  mu[FeO],J/mol  nom_ox
min      2.00712       -759753.       0.444856       0.106776E+007   355919.        5.99739        7.20797        3.46259
2.08167        2968.57       -836883.        66.1735        0.136719E-004  0.910063E-006   88.5907        26.6567        60.0840
-56.3128       -18.7709        4.06906        1.35635       -0.115099E-003 -0.138332E-003 -0.664524E-004  0.842941E-005
0.101309E-004  0.486672E-005   1.00452        25.1614        23.2477        61.6539        0.00000        0.00000        0.00000
1.00000        0.00000        0.00000        0.00000        0.00000        0.00000        0.00000       -715843.       -614521.       -
0.158423E+007  -836883.       -757981.       -731966.       -886966.       -459392.       -289429.        0.00000
max      2.02400       -734710.       0.460753       0.110380E+007   367932.        6.07227        7.29796        3.50583
2.08167        2993.55       -808935.        69.3182        0.143563E-004  0.941797E-006   101.562        30.2996        60.0840
-54.8038       -18.2679        4.10270        1.36757       -0.109235E-003 -0.131284E-003 -0.630670E-004  0.869790E-005
0.104536E-004  0.502174E-005   1.00561        27.8008        26.1582        66.0965        0.00000        0.00000        0.00000
1.00000        0.00000        0.00000        0.00000        0.00000        0.00000        0.00000       -680243.       -600647.       -
0.155172E+007  -808935.       -695283.       -707645.       -857553.       -408649.       -265010.        0.00000

Output has been written to the 2d tab format file: ex12_3.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
```

Open the ex12_3.tab file using Excel and search the column reporting the amount of Si in coesite. Copy and paste this column in the ex12_2.tab file, in order to add the compositional data for coesite in the Werami input file. Rename the modified file as ex12_2_mod.tab.

(2) User's .txt file

The .txt input file must contain:

(i) As many rows of comment text as wanted, just make sure they start with ‘#’; these will not be read by the script, and can contain information about the sample or the calculation

(ii) Any given name for the considered element; these will serve as titles for the plots and the saved .pdf files

(iii) The measured composition (in a.p.f.u.) for each element corresponding to the WERAMI calculation. **Note that, to avoid numerical issues in the calculations, the measured Si in coesite must be fixed at 1.001 a.p.f.u.**

(iv) The observed uncertainty (1σ) for each element; alternatively, “-“ must be inserted to let the script calculate an uncertainty based on the type of acquired analysis

(v) Type of analysis: EDS, WDS map, WDS spot

(vi) The name of the phases; these will serve as titles for the plots and the saved .pdf files

(vii) A chosen colour scheme for the plots from the options available in Python

```
# text
#
# Report uncertainties under each a.p.f.u. value, or let IntersecT calculate an uncertainty based on the type of measurement.
# Report the type of measurement: EDS, WDS map, WDS spot
#
# Examples of available colour schemes: viridis, plasma, inferno, magma, cividis, copper, spring
#
#
# Sample name: DM1707

Grt_Mg Grt_Ca Grt_Mn Grt_Fe Ctd_Mg Ctd_Fe Wm_Mg  Wm_Fe  Wm_Si  Wm_Al  Coe_Si
0.277  0.150  0.090  2.460  0.228  0.747  0.400  0.096  3.496  2.054  1.001
-
EDS

Phases:
Grt  Ctd  Wm   Coe

Colour scheme:
jet
```

How to run IntersecT

IntersecT requires Python v3.10 or more recent versions

Install Jupyter Notebook. Run the following to install:

```
pip install jupyterlab
pip install notebook
```

Download the Intersect Jupyter Notebook file and save it in the Python\Scripts directory.

In the Python\Scripts directory, double-click on the **jupyter-notebook.exe** file - it will open a browser tab which is a local folder - and run the **IntersecT.ipynb** file
Alternatively, use any code editor (e.g., Visual Studio Code) and open the **IntersecT.ipynb** file.

Read the instructions and run the code cells (**Shift+Enter** when positioned in the cell, or **Run all**)

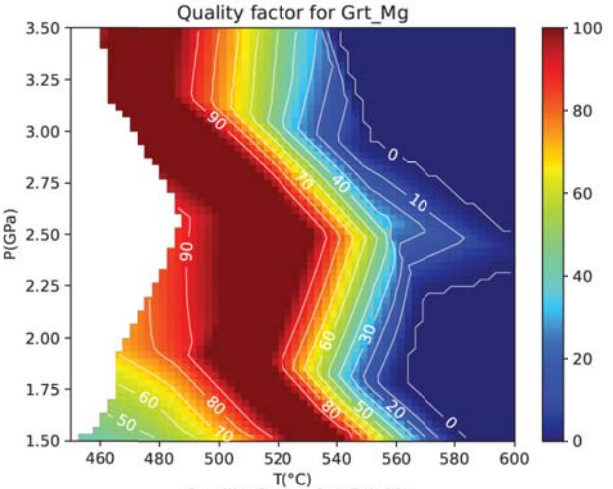
IntersecT asks you to import the output file from PerpleX (i.e. the .tab file created by WERAMI) and the .txt file with the measured mineral compositions and to select the output directory. For each of these points, a new window will open, which might remain hidden below the main one.

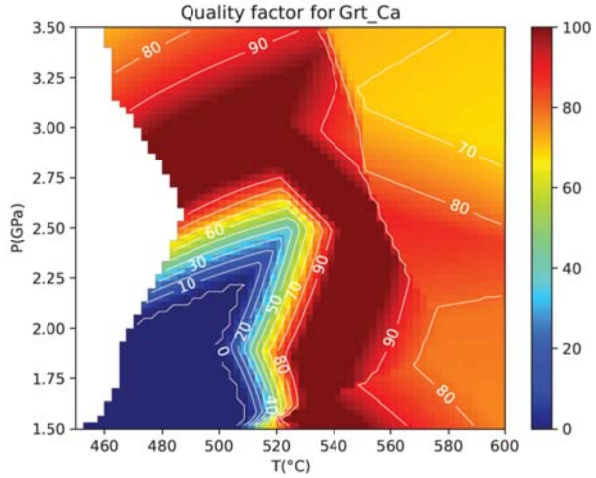
Then, IntersecT starts working, by calculating:

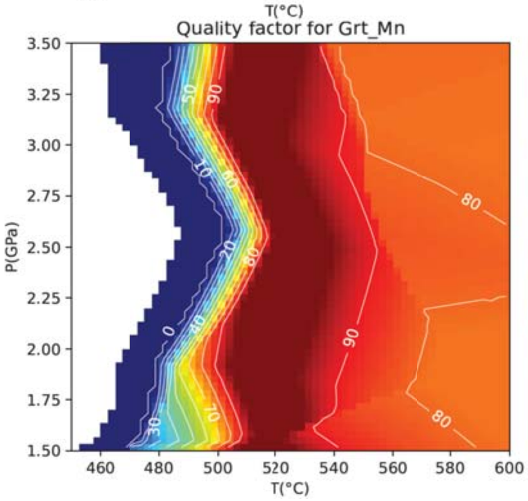
(1) The quality factor for each element in each phase (e.g. Mg in garnet, Ca in garnet, etc.)
(2) The quality factor for each phase (Grt, Cld, Phe, Coe)
(3) The reduced χ2 (or simple χ2) statistic for each phase (Grt, Cld, Phe, Coe) and for the overall dataset
(4) The unweighted and weighted total quality factor for the overall dataset

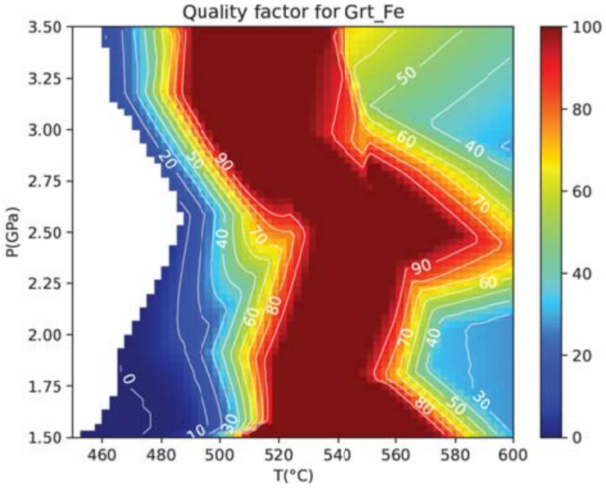
For each of these steps, punctual values are reported as printed text in the cells, e.g., the maximum Q_{cmp} values for each calculation.

(1a) Quality factor for each element in garnet









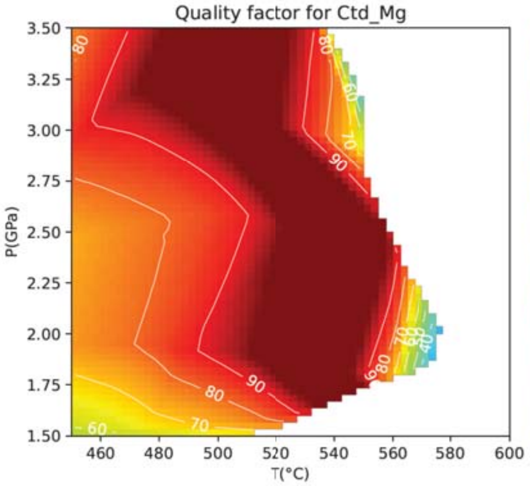
The maximum value of the quality factor for Grt_Mg is: 100.0

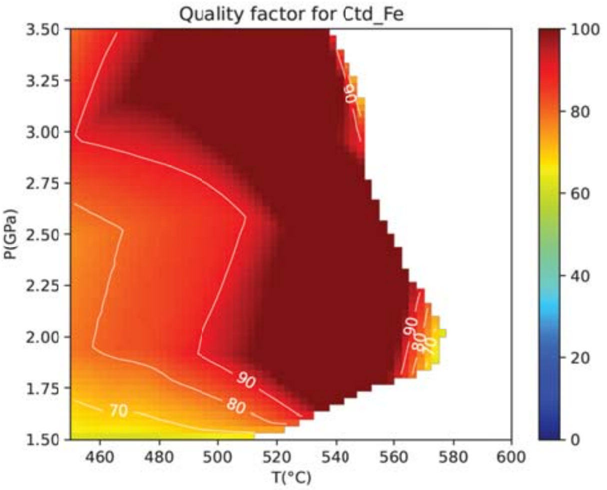
The maximum value of the quality factor for Grt_Ca is: 100.0

The maximum value of the quality factor for Grt_Mn is: 100.0

The maximum value of the quality factor for Grt_Fe is: 100.0

(1b) Quality factor for each element in chloritoid

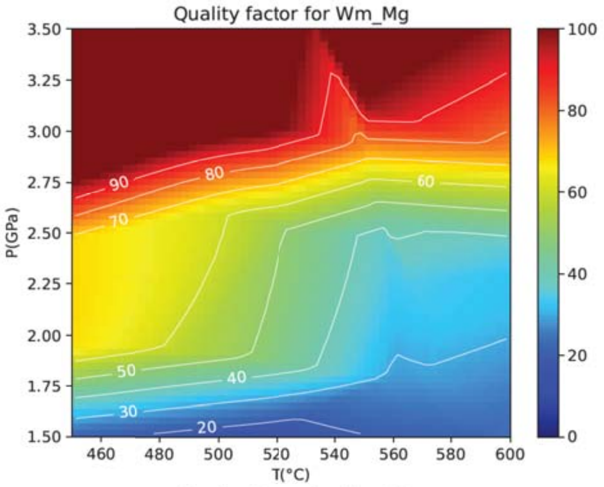


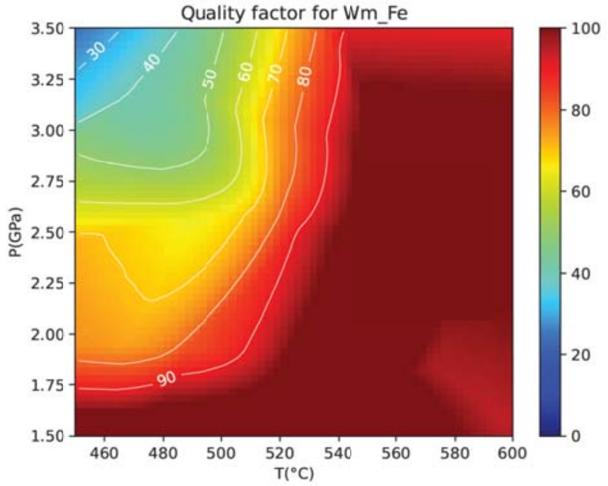


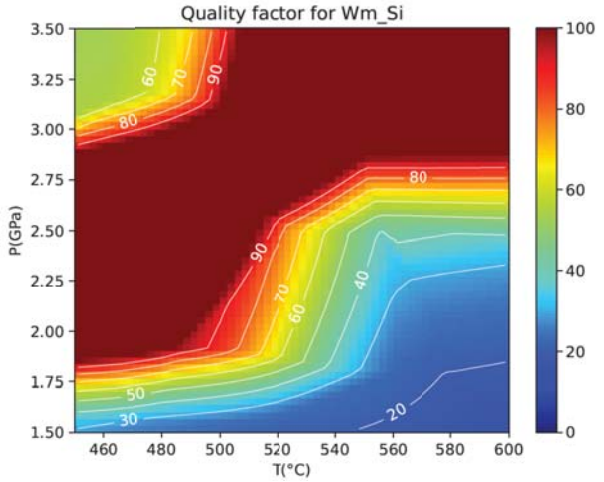
The maximum value of the quality factor for Ctd_Mg is: 100.0

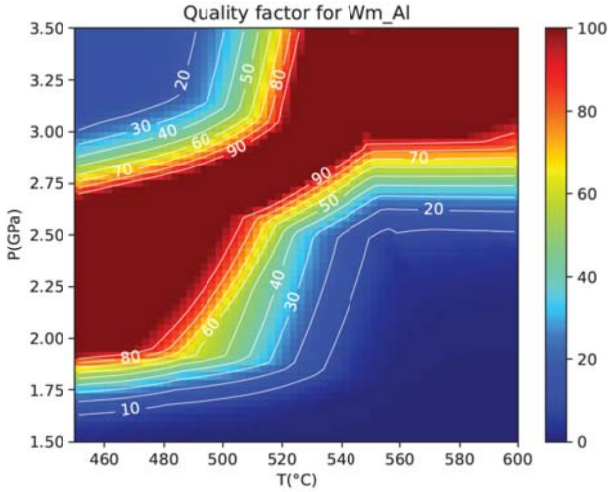
The maximum value of the quality factor for Ctd_Fe is: 100.0

(1c) Quality factor for each element in phengite









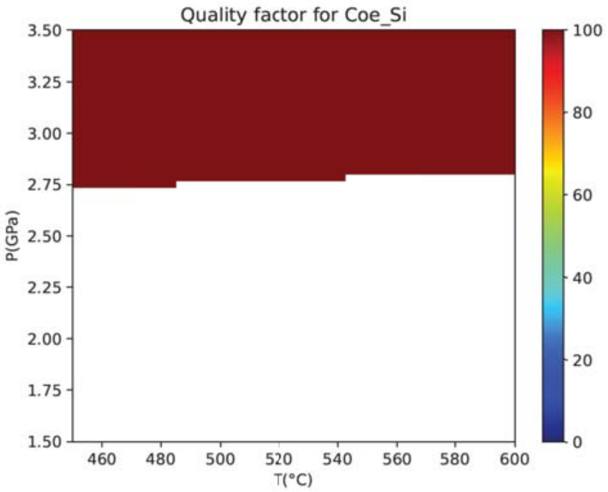
The maximum value of the quality factor for Wm_Mg is: 100.0

The maximum value of the quality factor for Wm_Fe is: 100.0

The maximum value of the quality factor for Wm_Si is: 100.0

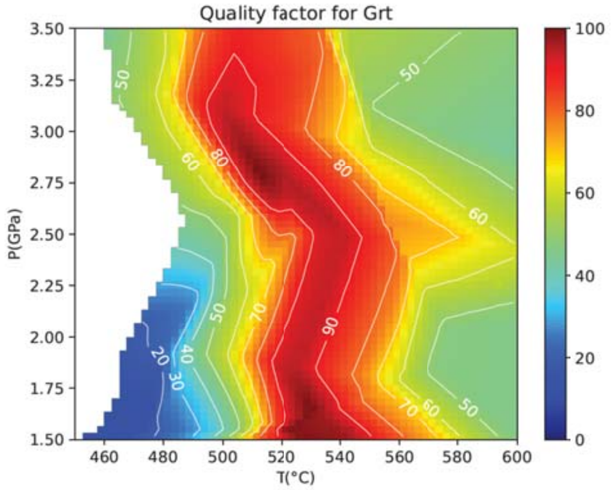
The maximum value of the quality factor for Wm_Al is: 100.0

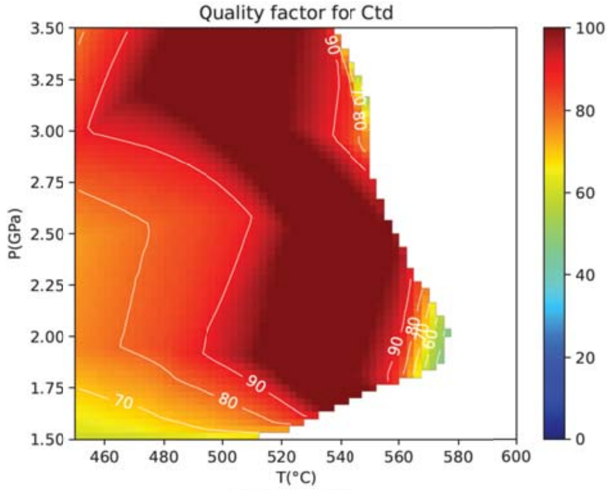
(1d) Quality factor for Si in coesite

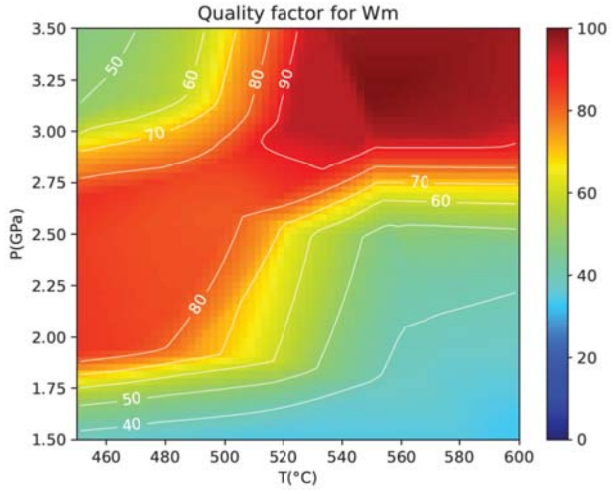


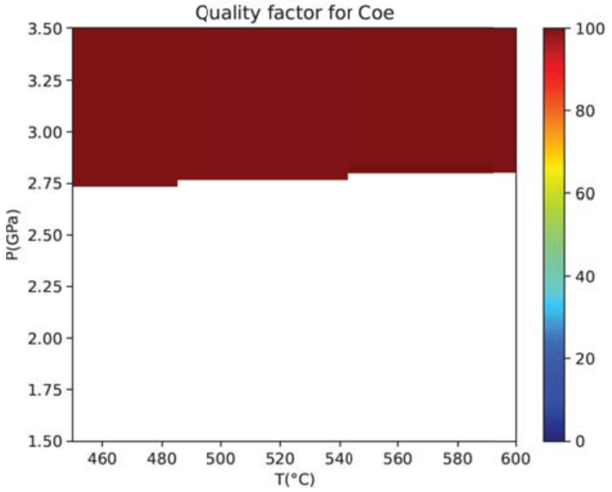
The maximum value of the quality factor for Coe_Si is: 100.0

(2) Quality factor for each phase (garnet, chloritoid, phengite, coesite)







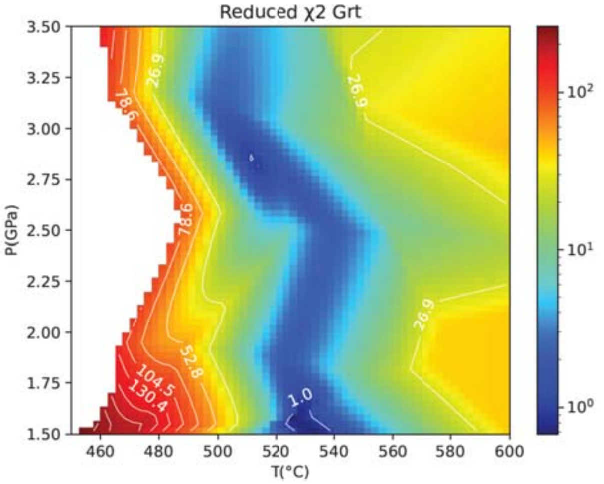


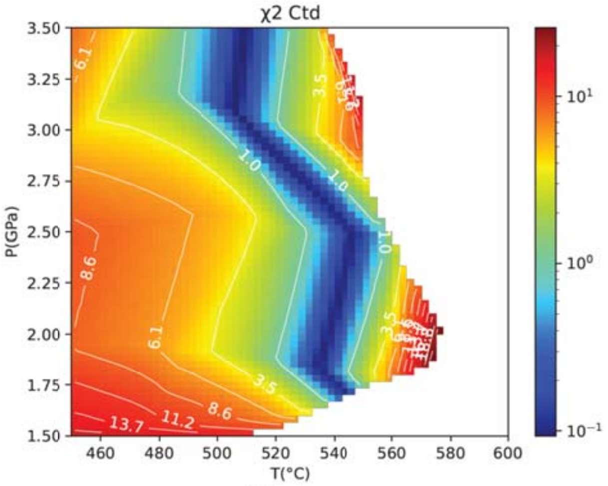
The maximum value of the quality factor for Grt is: 99.77590708084475
The T(°C) and P(GPa) position of the maximum Qcmp of Grt is: [513.559] , [2.78814]

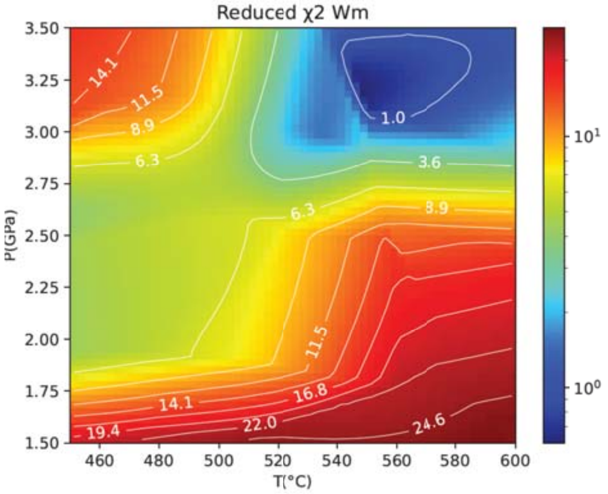
The maximum value of the quality factor for Ctd is: 100.0
The maximum value of the quality factor for Wm is: 100.0

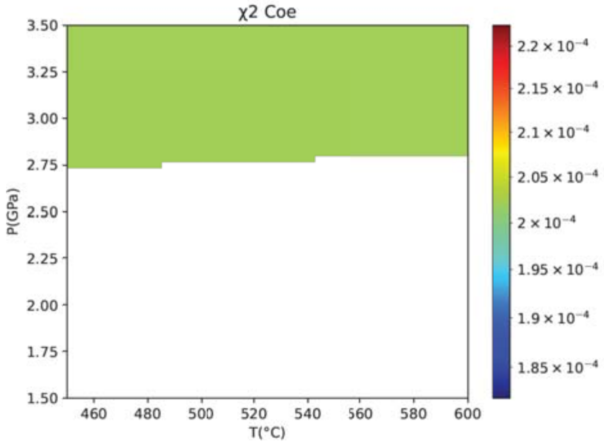
The maximum value of the quality factor for Coe is: 100.0

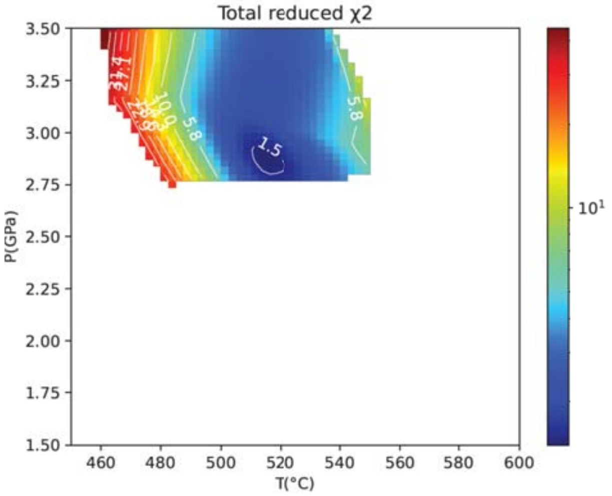
(3) Reduced χ2 statistic for each phase and for the overall dataset











The number of elements in Grt is: 4.

The minimum reduced χ2 value for Grt is: 0.6776523272607262

The number of elements in Ctd is: 2

The minimum χ2 value for Ctd is: 0.09362670385854904

The number of elements in Wm is: 4

The minimum reduced χ2 value for Wm is: 0.6045625770960417

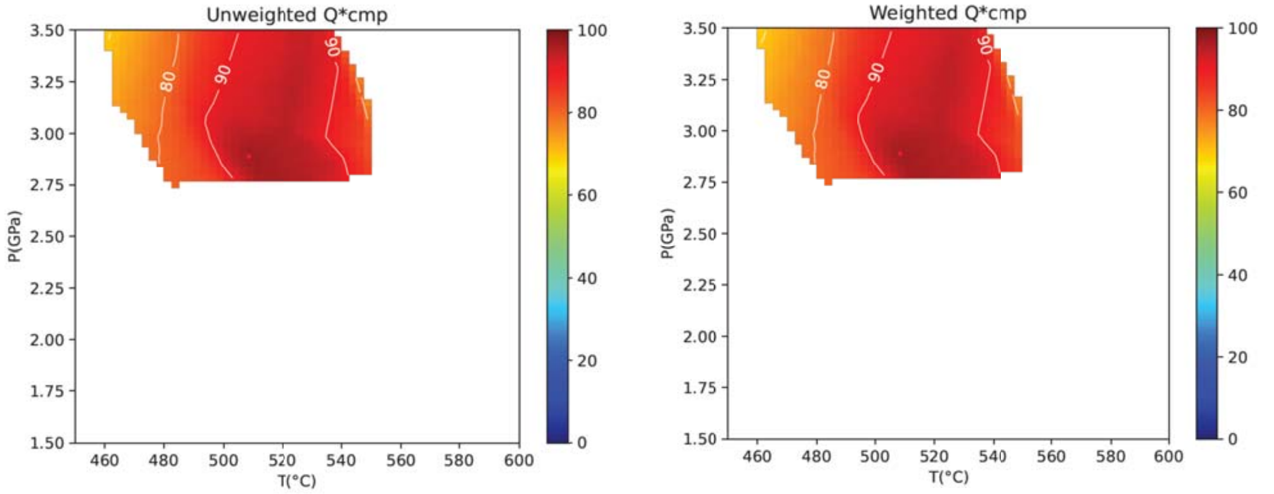
The number of elements in Coe is: 1

The minimum χ2 value for Coe is: 0.00020219903164758396

The minimum value of the total reduced χ2 is: 1.4013716912787582

The T(°C) and P(GPa) position of the minimum total reduced χ2 is: [516.102] , [2.85593]

(4) The unweighted and weighted total quality factor for the overall dataset



Unweighted quality factor for the overall dataset

The reduced χ2 values for the phases at the maximum Q*cmp is: [1.06888939e+00 9.96700645e-01 3.99170308e+00 2.02199032e-04]

The maximum value of the Q*cmp is: 96.58056965569587

The T(°C) and P(GPa) position of the maximum Q*cmp is: 508.475 , 2.88983

Weighted quality factor for the overall dataset

The weight is: [1.   0.91438879 1.   0.99979784]

The normalized weight fraction is: [0.25548092 0.23360889 0.25548092 0.25542927]

The reduced χ2 values for the phases at the maximum Q*cmp are: [1.06888939e+00 9.96700645e-01 3.99170308e+00 2.02199032e-04]

The maximum value of the Q*cmp is: 96.50560316644186

The T(°C) and P(GPa) position of the maximum Q*cmp is: 508.475 , 2.88983

NOTE: Because chloritoid has a χ2 > 0, i.e. slightly higher than the best fit for the χ2, its weight will be lower than that of the other phases.

The results obtained from IntersecT confirm the P-T estimates obtained using the qualitative isopleth thermobarometry approach (i.e., 500-515 °C, 2.7-3.0 GPa) and provide a quantitative assessment of the quality of fit between the modelled and the observed mineral compositions.

Ex 13

Ex. 13 – DIRECT modelling of an anatectic METAPELITE (NKCFMASH system)

This exercise deals with the "DIRECT" modelling of a metapelite sample at supra-*solidus* conditions (i.e. melt-bearing). "Direct modelling" means that you know which is the protolith composition, <u>including its initial H_2O amount</u> (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. (2007) [J. metam. Geol., 25, 511-527]. The P-T pseudosection is reported in their Fig. 6.

Bulk composition (mol%):

SiO2=70.09, Al2O3=8.95, FeO=6.93, MgO=3.64, CaO=0.28, Na2O=0.57, K2O=2.87, H2O=6.66

T=630-1000°C

P=0-12 kbar

(1) Definition of the problem (BUILD)

```
C:\PERPLEX\Perplex7110>build

Perple_X release 7.1.10 Dec 21, 2024.
Copyright (C) 1986-2024 James A D Connolly <www.perplex.ethz.ch/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]:
ex13

The problem definition file will be named: ex13.dat

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

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
6 - 0-d Infiltration-reaction-fractionation
7 - 2-d Phase fractionation (FRAC2D and TITRATE reactive transport models)
8 - (pseudo-)Ternary liquidus/solidus surfaces
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)?
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 CO2 CuO Cr2O3 S2 F2 N2 ZnO
Enter names, 1 per line, press <enter> to finish:
Na2O
MgO
Al2O3
SiO2
K2O
CaO
FeO
H2O

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         20     20        20 x  20 nodes
auto-refine      4         60     60       473 x 473 nodes
To change these options edit or create the file perplex_option.dat
See: www.perplex.ethz.ch/perplex_options.html#grid_parameters

Specify component amounts by mass (Y/N)?
n
The amounts you enter next need not be normalized; regardless of units, they define the molar amount of
the system

Enter the molar amounts of the components:
 Na2O  MgO   Al2O3 SiO2 K2O   CaO   FeO   H2O
for the bulk composition of interest:
0.57
3.64
8.95
70.09
2.87
0.28
6.93
6.66

Output a print file (Y/N)?
y

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
clinohumite models:      TiCh(PL)   Chum
```

```
ternary-feldspar models:  feldspar   feldspar_B Pl(I1,HP)  Fsp(C1)    Fsp(HGP21)
…
For details on these models 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:
Ex13
```

(2) Doing the calculation (VERTEX)

Run VERTEX to make the calculation:

```
C:\PERPLEX\Perplex7110>vertex

Perple_X release 7.1.10 Dec 21, 2024.
Copyright (C) 1986-2024 James A D Connolly <www.perplex.ethz.ch/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\Perplex7110>pssect

Perple_X release 7.1.10 Dec 21, 2024.
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Enter the project name (the name assigned in BUILD) [default = my_project]:
ex13

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)
```
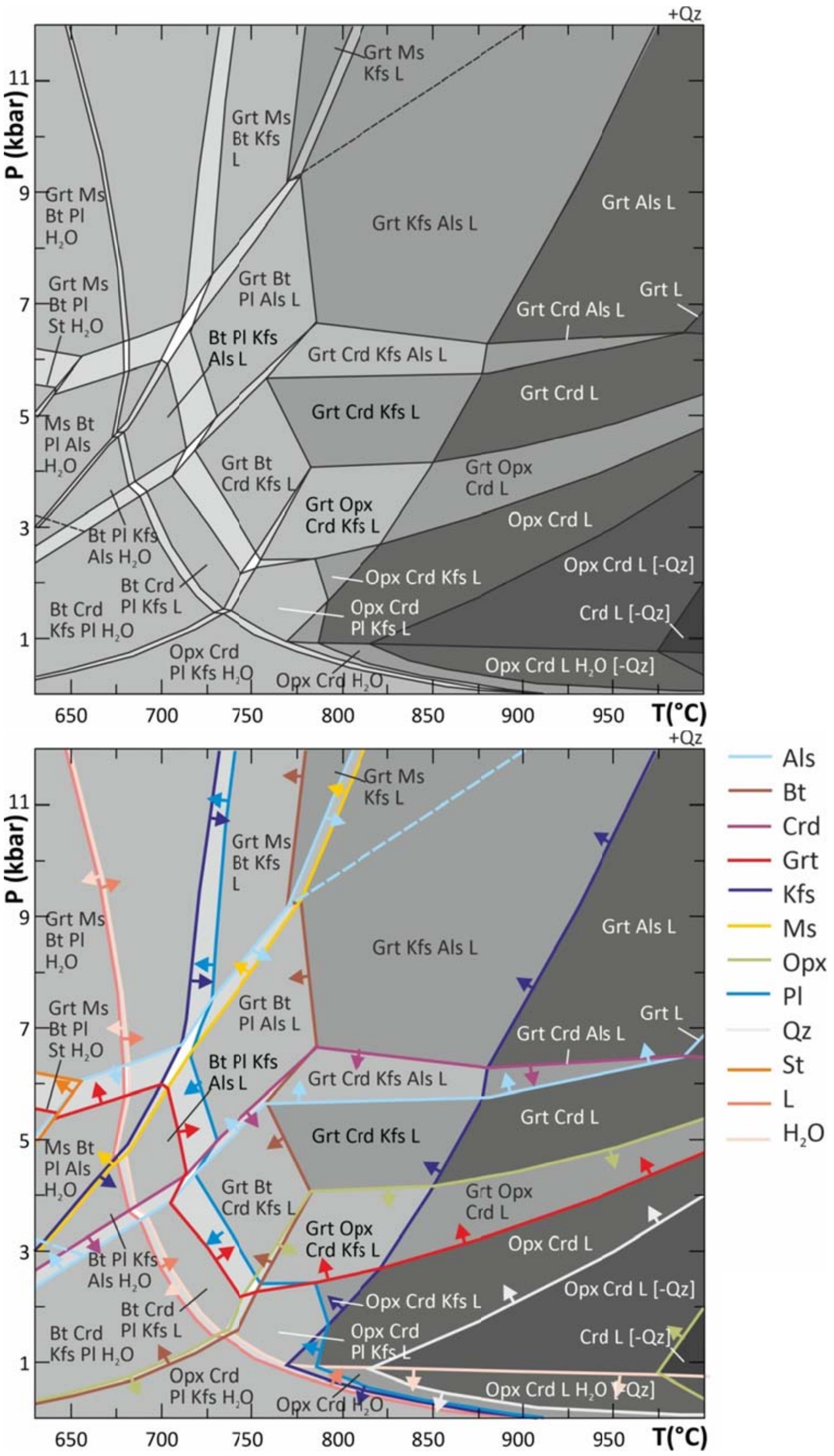

```
   contour_t_interval      50.00    >0 [50.0]
   contour_p_interval    1000.00    >0 [1000.0]
   field_fill            T         [T] F
   field_label           T         [T] F
   numeric_field_label   F         [F] T, if T PSSECT writes list to *_assemblages.txt
   replicate_label       0.250      0->1 [0.025]
   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
   splines               T         [T] F
   tenth_ticks           F         [F] T
   text_scale            1.000      [1.] (rel)
   plot_extra_data       F         [T] F, to plot, e.g., experimental observations
To change these options edit or create the plot option file See: www.perplex.ethz.ch/perplex_plot_options.html

PostScript will be written to file: ex13.ps

Modify the default plot (y/n)?
n

There are  10 fields for: Bio Crd Opx Fsp Fsp q H2O
There are   5 fields for: Bio Mica Fsp Fsp sill q H2O
There are  24 fields for: Bio Mica Gt Fsp Melt q H2O
There are   2 fields for: Bio Mica Gt Fsp Melt sill q
There are   4 fields for: Bio Gt Crd Fsp Fsp Melt sill q
There are   2 fields for: Bio Mica Gt Fsp Fsp Melt sill q
There are  12 fields for: Crd Opx Fsp Fsp Melt q H2O
There are   3 fields for: Bio Gt Crd Opx Fsp Melt q
There are   2 fields for: Mica Gt Fsp Melt sill q
There are   5 fields for: Crd Opx Fsp Melt trd H2O
There are   2 fields for: Bio Mica Gt St Fsp sill q H2O
```

+Qz
P (kbar)
T(°C)
650
700
750
800
850
900
950
1
3
5
7
9
11
Grt Ms Kfs L
Grt Ms Bt Kfs L
Grt Ms Bt Pl H$_2$O
Grt Kfs Als L
Grt Als L
Grt Bt Pl Als L
Grt Ms Bt Pl St H$_2$O
Grt L
Grt Crd Als L
Bt Pl Kfs Als L
Grt Crd Kfs Als L
Grt Crd L
Ms Bt Pl Als H$_2$O
Grt Crd Kfs L
Grt Bt Crd Kfs L
Grt Opx Crd L
Grt Opx Crd Kfs L
Opx Crd L
Bt Pl Kfs Als H$_2$O
Opx Crd Kfs L
Opx Crd L [-Qz]
Bt Crd Pl Kfs L
Bt Crd Kfs Pl H$_2$O
Opx Crd Pl Kfs L
Crd L [-Qz]
Opx Crd Pl Kfs H$_2$O
Opx Crd H$_2$O
Opx Crd L H$_2$O [-Qz]
Als
Bt
Crd
Grt
Kfs
Ms
Opx
Pl
Qz
St
L
H$_2$O

(4) Calculating ISOMODES (WERAMI)

This section explains how to calculate 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\Perplex7110>werami

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Enter the project name (the name assigned in BUILD) [default = my_project]:
ex13

Reading Perple_X options from: perplex_option.dat
Writing Perple_X option summary to: 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] 0-150
    aq_solvent_composition  y         [y] m: y => mol fraction, m => molality
    aq_solute_composition   m         y [m]: y => mol fraction, m => molality
    spreadsheet             T         [T] F
    logarithmic_p           F         [F] T
    logarithmic_X           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           T         [T] F
    solution_names          abb       [model] abbreviation full
    structural_formulae     T         [T] F
    output_species          T         [T] F
    output_species_props    F         [F] T
    seismic_output          som       [some] none all
    poisson_test            F         [F] T
    interim_results         aut       [auto] off manual
    sample_on_grid          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
    finite_strain_alpha    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      [2] >0
    finite_difference_p    1.0E+04  [1d4] >0; fraction = 1.0E-03   [1d-3]
  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
    fluid_shear_modulus    T        [T] F
    phi_d                  0.36     [0.36] 0->1
  Error/warning control options:
    pause_on_error         T        [T] F
    max_warn_limit         5        [5]
    warn_interactive       T        [T] F
    aq_error_ver100        F        [F] T, abort during iteration
    aq_error_ver101        T        [T] F, solute undersaturation abort
    aq_error_ver102        T        [T] F, pure + impure solvent abort
    aq_error_ver103        T        [T] F, out-of-range HKF g abort
    aq_error_ver104        T        [T] F, abort on failed respeciation
    warning_ver637         T        [T] F
    error_ver109           T        [T] F
    do_not_reset_options   F        [F] T, prevents automatic resets
To change these options see: www.perplex.ethz.ch/perplex_options.html
--------------------------------------------------------------------------------
Select operational mode:
    1 - properties at specified conditions
    2 - properties on a 2d grid
    3 - properties along a 1d path
    4 - as in 3, but input from file
    0 - EXIT
2

Select a property:
   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)
Fractions are Wt, Vol, or Mol depending on the perplex_option.dat proportions keyword.

Select an additional property or enter 0 to finish:
7
Enter solution or compound (left justified):
Mica(W)
Include fluid in computation of aggregate (or modal) properties (y/n)?
y
Fractions are Wt, Vol, or Mol depending on the perplex_option.dat proportions keyword.

Select an additional property or enter 0 to finish:
7
Enter solution or compound (left justified):
```

```
Bi(W)
Include fluid in computation of aggregate (or modal) properties (y/n)?
y
Fractions are Wt, Vol, or Mol depending on the perplex_option.dat proportions keyword.

Select an additional property or enter 0 to finish:
7
Enter solution or compound (left justified):
q
Include fluid in computation of aggregate (or modal) properties (y/n)?
y
Fractions are Wt, Vol, or Mol depending on the perplex_option.dat proportions keyword.

Select an additional property or enter 0 to finish:
7
Enter solution or compound (left justified):
feldspar
Include fluid in computation of aggregate (or modal) properties (y/n)?
y
Fractions are Wt, Vol, or Mol depending on the perplex_option.dat proportions keyword.

Select an additional property or enter 0 to finish:
7
Enter solution or compound (left justified):
Gt(W)
Include fluid in computation of aggregate (or modal) properties (y/n)?
y
Fractions are Wt, Vol, or Mol depending on the perplex_option.dat proportions keyword.

Select an additional property or enter 0 to finish:
7
Enter solution or compound (left justified):
Crd(W)
Include fluid in computation of aggregate (or modal) properties (y/n)?
y
Fractions are Wt, Vol, or Mol depending on the perplex_option.dat proportions keyword.

Select an additional property or enter 0 to finish:
7
Enter solution or compound (left justified):
Opx(W)
Include fluid in computation of aggregate (or modal) properties (y/n)?
y
Fractions are Wt, Vol, or Mol depending on the perplex_option.dat proportions keyword.

Select an additional property or enter 0 to finish:
7
Enter solution or compound (left justified):
```

```
ky
Include fluid in computation of aggregate (or modal) properties (y/n)?
y
Fractions are Wt, Vol, or Mol depending on the perplex_option.dat proportions keyword.

Select an additional property or enter 0 to finish:
7
Enter solution or compound (left justified):
sill
Include fluid in computation of aggregate (or modal) properties (y/n)?
y
Fractions are Wt, Vol, or Mol depending on the perplex_option.dat proportions keyword.

Select an additional property or enter 0 to finish:
7
Enter solution or compound (left justified):
and
Include fluid in computation of aggregate (or modal) properties (y/n)?
y
Fractions are Wt, Vol, or Mol depending on the perplex_option.dat proportions keyword.

Select an additional property or 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 [default]
   2 -  119 x  119 nodes
   3 -  237 x  237 nodes
   4 -  473 x  473 nodes
4
**warning ver538** use of multi-level grids may generate noise due to data interpolation onto unpopulated nodes. If
exceptional resolution is required set grid_levels to 1 1 and change the 2nd value of x/y_nodesto obtain the desired
resolution.
To disable [all] interactive warnings set warn_interactive to F.

Continue (y/n)?
y
…
…

2 immiscible phases of feldspar
coexist with the following molar  compositions:
   Na2O    MgO     Al2O3   SiO2    K2O     CaO     FeO     H2O
    0.073   0.000   0.505   2.990   0.422   0.010   0.000   0.000
    0.206   0.000   0.785   2.430   0.009   0.570   0.000   0.000
```

Current conditions:
    T(K)   =   903.0000
    P(bar)   = 0.1000000

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** Stable immiscibility is predicted by the following solution models:
   feldspar
Interpolation will be turned off at all affected nodes. To override this behavior at the risk of computing inconsistent
properties set warning_ver637 to F and restart WERAMI.

Data ranges excluding values equal to bad_number (       NaN) specified in perplex_option.dat:
    melt(W),vo%    Mica(W),vo%    Bi(W),vo%      q,vo%         feldspar,vo%   Gt(W),vo%      Crd(W),vo%      Opx(W),vo%
ky,vo%        sill,vo%       and,vo%
min   0.124322E-002  0.232922E-001  0.821043E-003  0.241205E-003  0.176327E-004  0.116329E-002  0.129966E-002
0.304364E-003  0.107932E-002  0.158178E-003  0.283109E-001
max    82.3463       29.4303       27.3946       50.4189       18.7902       18.5521       22.9178       7.95602       3.45585
8.09854       8.24995

Output has been written to the 2d tab format file: ex13_1.tab

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

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

At the end, you have a new file (ex13_1.tab) in the Perple_X folder.

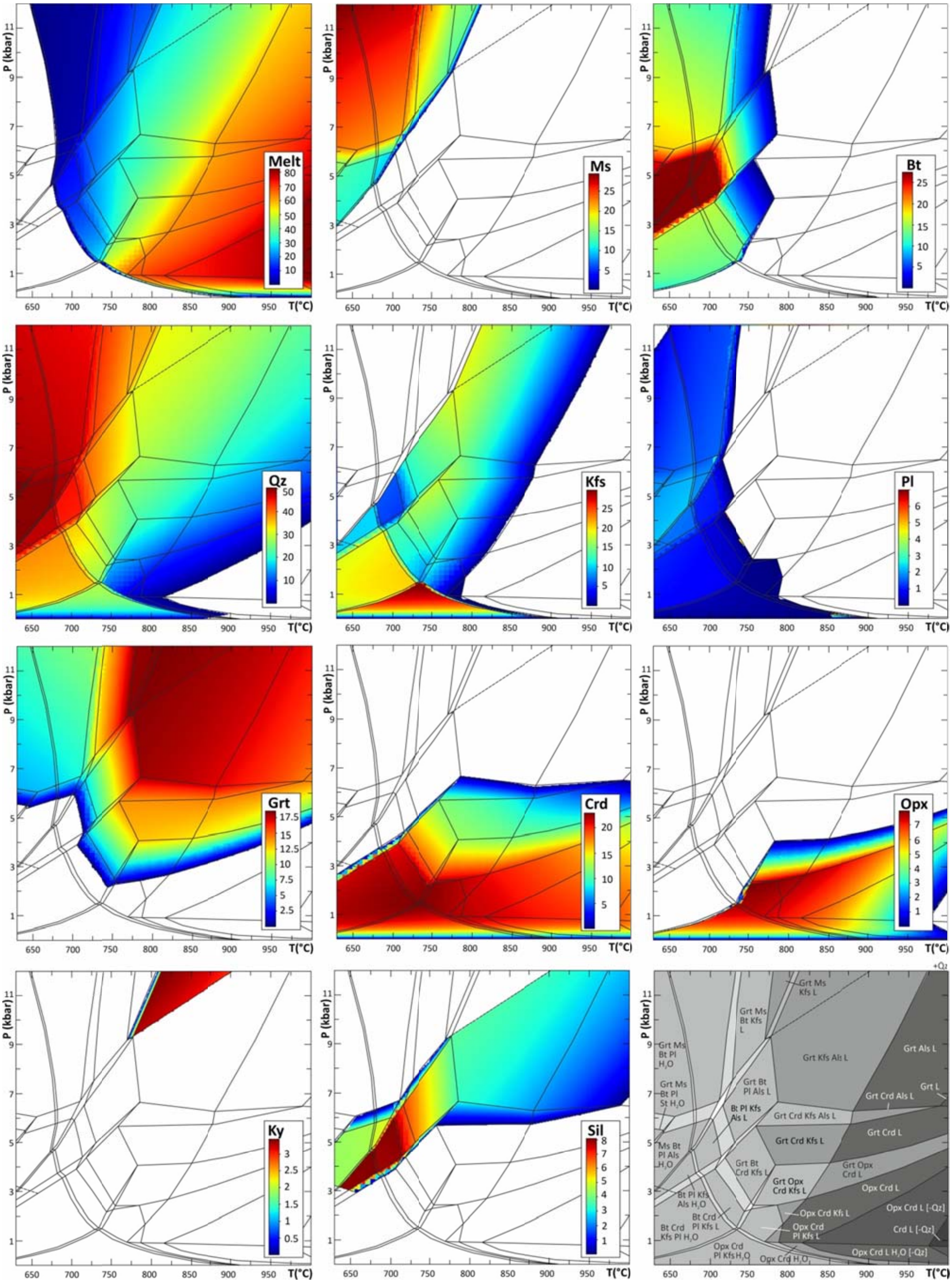
Run again WERAMI to calculate isomodes for K-feldspar (ex13_3.tab).

NB: If you have doubts on which feldspar is stable in each field assemblage, you can run WERAMI, option 1. This option allows to calculate all the properties of the system (including phase compositions) at specified P-T conditions.

For example at **973 K (700°C), 8 kbar**:

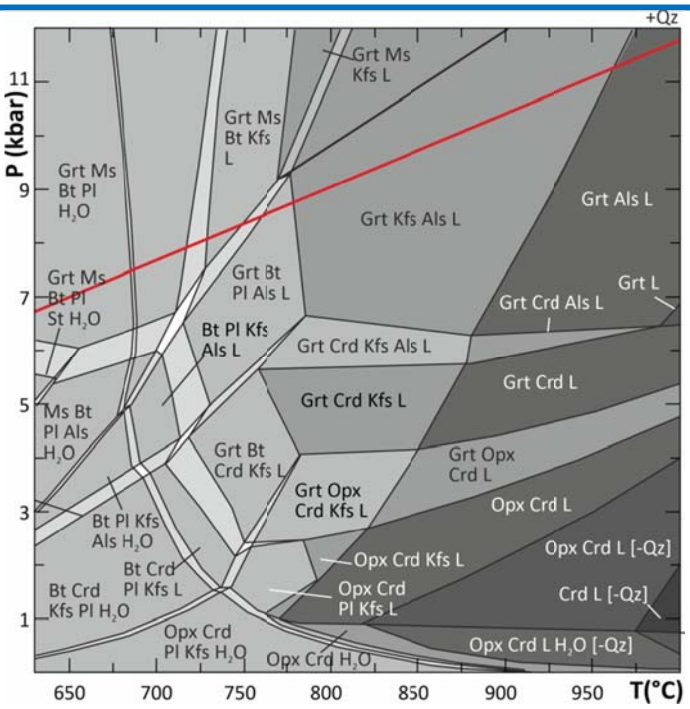
```
Stable phases at:
```

```
            T(K)    =  973.000
            P(bar)  =  8000.00

Phase Compositions (molar  proportions):
        wt %    vol %   mol %   mol      Na2O     MgO      Al2O3    SiO2     K2O      CaO      FeO      H2O
 Bio     16.90   15.73   4.17    2.26    0.00000  1.19640  0.79431  2.70569  0.50000  0.00000  1.50928  1.00000
 Mica     23.41   23.48   6.75    3.65    0.04019  0.05211  1.39947  3.09889  0.45817  0.00327  0.05006  1.00000
 Gt      10.84    7.44   2.60    1.40    0.00000  0.53419  1.00000  3.00000  0.00000  0.08768  2.37813  0.00000
 Fsp      3.60    3.89   1.56   0.842    0.39154  0.00000  0.58332  2.83337  0.02514  0.16663  0.00000  0.00000
 Melt     1.93    2.56   2.15    1.16    0.08063  0.00117  0.13556  1.13041  0.04252  0.00404  0.00382  0.65004
 q       43.32   46.89  82.78    44.8    0.00000  0.00000  0.00000  1.00000  0.00000  0.00000  0.00000  0.00000

Phase speciation (molar proportions):
 Bio      east: 0.29431, ann: 0.52221, phl: 0.24082, obi: -0.05735
 Mica      mu: 0.81418, pa: 0.08038, ma1_dqf: 0.00327, cel: 0.05211, fcel: 0.05006
 Gt      alm: 0.79271, py: 0.17806, gr: 0.02923
 Fsp      abh: 0.78308, an: 0.16663, san: 0.05029
 Melt      fo8L: 0.00029, fa8L: 0.00095, abL: 0.16127, sil8L: 0.00522, anL: 0.00404, kspL: 0.08505, q8L: 0.09313
        h2oL: 0.65004
```


P (kbar)
T(°C)
1
3
5
7
9
11
650
700
750
800
850
900
950
Melt
10
20
30
40
50
60
70
80
Ms
5
10
15
20
25
Bt
5
10
15
20
25
Qz
10
20
30
40
50
Kfs
5
10
15
20
25
Pl
1
2
3
4
5
6
Grt
2.5
5
7.5
10
12.5
15
17.5
Crd
5
10
15
20
Opx
1
2
3
4
5
6
7
Ky
0.5
1
1.5
2
2.5
3
Sil
1
2
3
4
5
6
7
8
+Qz
Grt Ms Kfs L
Grt Ms Bt Kfs L
Grt Ms Bt Pl H₂O
Grt Ms Bt Pl St H₂O
Ms Bt Pl Als H₂O
Grt Kfs Als L
Grt Als L
Grt Bt Pl Als L
Grt L
Grt Crd Als L
Bt Pl Kfs Als L
Grt Crd Kfs Als L
Grt Crd L
Grt Crd Kfs L
Grt Bt Crd Kfs L
Grt Opx Crd L
Grt Opx Crd Kfs L
Opx Crd L
Bt Pl Kfs Als H₂O
Opx Crd L [-Qz]
Opx Crd Kfs L
Bt Crd Pl Kfs L
Opx Crd Pl Kfs L
Crd L [-Qz]
Bt Crd Kfs Pl H₂O
Opx Crd Pl Kfs H₂O
Opx Crd H₂O
Opx Crd L H₂O [-Qz]

(5) Calculating CUMULATIVE MODES along a prograde path (WERAMI)

This section illustrates how to calculate the **variation in the modal amounts** of all the phases (vol%) along a prograde path defined as: P (bar) = 13.33 T (K) – 5306.67 (corresponding to the red line reported below). The exercise is similar to Ex. 10.



Run WERAMI to calculate the ISOMODES of each phase.

```
C:\PERPLEX\Perplex7110>werami

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Enter the project name (the name assigned in BUILD) [default = my_project]:
ex13

Reading Perple_X options from: perplex_option.dat
Writing Perple_X option summary to: 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] 0-150
    aq_solvent_composition  y        [y] m: y => mol fraction, m => molality
    aq_solute_composition   m        y [m]: y => mol fraction, m => molality
    spreadsheet            T        [T] F
    logarithmic_p          F        [F] T
    logarithmic_X          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           T         [T] F
  solution_names          abb       [model] abbreviation full
  structural_formulae     T         [T] F
  output_species          T         [T] F
  output_species_props    F         [F] T
  seismic_output          som       [some] none all
  poisson_test            F         [F] T
  interim_results         aut       [auto] off manual
  sample_on_grid          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
  finite_strain_alpha     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       [2] >0
  finite_difference_p     1.0E+04   [1d4] >0; fraction = 1.0E-03   [1d-3]
 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
  fluid_shear_modulus     T         [T] F
  phi_d                   0.36      [0.36] 0->1
 Error/warning control options:
  pause_on_error          T         [T] F
  max_warn_limit          5         [5]
  warn_interactive        T         [T] F
  aq_error_ver100         F         [F] T, abort during iteration
  aq_error_ver101         T         [T] F, solute undersaturation abort
  aq_error_ver102         T         [T] F, pure + impure solvent abort
  aq_error_ver103         T         [T] F, out-of-range HKF g abort
  aq_error_ver104         T         [T] F, abort on failed respeciation
  warning_ver637          T         [T] F
  error_ver109            T         [T] F
  do_not_reset_options    F         [F] T, prevents automatic resets
To change these options see: www.perplex.ethz.ch/perplex_options.html
```

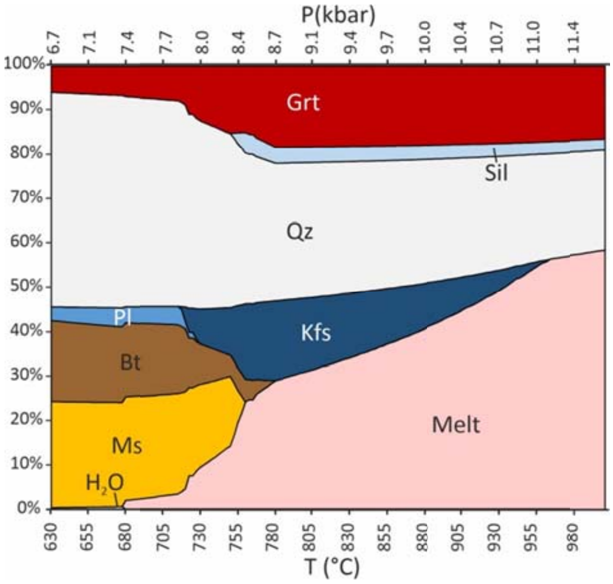
```
--------------------------------------------------------------------------------
Select operational mode:
    1 - properties at specified conditions
    2 - properties on a 2d grid
    3 - properties along a 1d path
    4 - as in 3, but input from file
3

Construct a non-linear profile (y/n)?
n

Enter endpoint 1 (T(K)    -P(bar)  ) coordinates:
903
6730.32

Enter endpoint 2 (T(K)    -P(bar)  ) coordinates:
1273
11662.42

How many points along the profile?
150

Select a property:
    1 - Specific Enthalpy (J/m3)
    2 - Density (kg/m3)
    3 - Specific heat capacity (J/K/m3)
    4 - Expansivity (1/K, for volume)
    5 - Compressibility (1/bar, for volume)
    6 - 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

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

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

**warning ver178** at T(K)=   903.0     P(bar)=   6730.
the shear modulus of: Bio
is missing or invalid and has been estimated with the poisson_ratio option
…
….**warning ver637** Stable immiscibility is predicted by the following solution models:
   feldspar
Interpolation will be turned off at all affected nodes. To override this behavior at the risk of computing inconsistent
properties set warning_ver637 to F and restart WERAMI.
…
To see how often this warning occurs increase max_warn_limit

Data ranges excluding values equal to bad_number (       NaN) specified in perplex_option.dat:
    Crd          Opx          Fsp          Fsp          q            H2O          Bio          and          Mica         sill         St           Gt
ab           Melt         ky           trd
min    0.100000E+100  0.100000E+100  0.229814      0.170749      22.6857      0.197698      0.402790
0.100000E+100   3.07168      2.37667      0.100000E+100  0.282971      0.100000E+100   3.49574      0.100000E+100
0.100000E+100
max   -0.100000E+100 -0.100000E+100   15.4323      9.71592      49.8381      0.903757      27.2947      -
0.100000E+100   11.9598      7.96009     -0.100000E+100   18.0271     -0.100000E+100   58.4177     -0.100000E+100 -
0.100000E+100

Output has been written to two files:
    plt format is in file: ex13_3.plt
    1d tab format is in file: ex13_3.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 (ex13_3.tab) in the Perple_X folder.

You can open the ex13_3.tab file using EXCEL; replace the NaN values with 0 and plot the data using the option Area Graph (see Ex10).

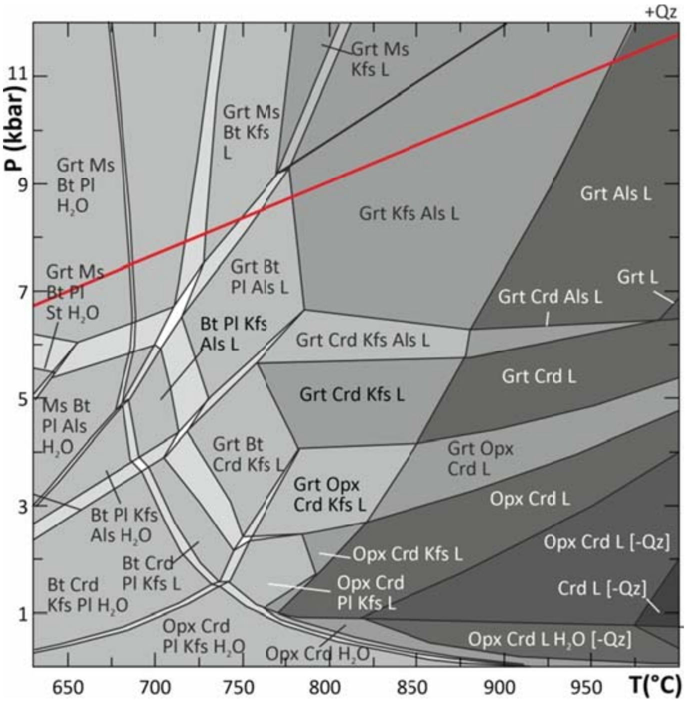


According to these results, more than 30 vol% of melt is produced at T>800°C. **This scenario is unrealistic**, because natural observations suggest that most migmatites and granulites have lost some to virtually all of their melt during metamorphism.

Ex 14

Ex. 14 – Modelling MELT FRACTIONATION (NKCFMASH system)

This exercise illustrates MELT FRACTIONATION CALCULATIONS for the same system investigated in Exercise 13. Melt fractionation is modelled along the prograde path reported in the figure below and defined as: P (bar) = 13.33 T(K) – 5306.67.



Fractionation details are defined by the following keywords in the perplex_option file:

- **1d_path** = number of points computed along the path. The default values are set to 40 and 160 points for the exploratory and autorefine cycles.
- **fractionation_hi_limit / fractionation_lo_limit** = these keywords permit specification of fractionation thresholds such that: 1) the mass fraction of a phase (melt, in this case) must exceed the fractionation_hi_limit before it is fractionated; and 2) the residual mass fraction of the phase (melt) after fractionation is fractionation_lo_limit. If fractionation_hi_limit ≤ fractionation_lo_limit, then VERTEX emulates Rayleigh fractionation, i.e., any fractionated phase is removed if its amount exceeds zero leaving no residual. Each keyword takes real values ≤ 1. The default for both keywords is zero.

Before starting to build the problem, **modify these keywords in the perplex_option file:**

```
fractionation_hi_limit  0.06  |[0.]  0-1,  upper  fractionation  threshold,mass
fraction
fractionation_lo_limit  0.005  |[0.]  0-1,  lower  fractionation  threshold,  mass
fraction
```

This means that: (1) each time the melt amount exceeds 6 wt%, melt is removed from the system and (2) after fractionation, a small amount of melt equal to 0.5 wt% remains in the system. **This approximates what is observed in nature, i.e. most migmatites and granulites have lost some to virtually all of their melt during metamorphism.**

The starting bulk composition, as well as the T (and P) range are the same as in Ex. 13.

(1) Definition of the problem (BUILD)

```
C:\PERPLEX\Perplex7110>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]:
ex14

The problem definition file will be named: ex12.dat

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

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
    6 - 0-d Infiltration-reaction-fractionation
    7 - 2-d Phase fractionation (FRAC2D and TITRATE reactive transport models)
    8 - (pseudo-)Ternary liquidus/solidus surfaces
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.
5
```

This is the option for phase fractionation calculation along a 1d path.

```
Calculations with a saturated fluid (Y/N)?
n
```

Comment as in Ex. 13.

```
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 CO2 CuO Cr2O3 S2  F2  N2 ZnO
Enter names, 1 per line, press <enter> to finish:
Na2O
MgO
Al2O3
SiO2
K2O
CaO
FeO
H2O

Enter path coordinates from a file (Y/N)?
n
```

In this case, we define the path using the equation: P (bar) = 13.33 T(K) – 5306.67

```
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)?

Answer yes to specify a P-T path for phase fractionation calculations.
y

Select dependent variable:
  1 - P(bar)   = f(T(K)    )
  2 - T(K)     = f(P(bar)  )
1

The dependence must be described by the polynomial
P(bar)   = Sum ( c(i) * [T(K)    ]^i, i = 0..n)
```

Paths are defined by a polynomial of the form
Y = c0 + c1 X1 + c2 X2 + ... + cn Xn
where Y is the dependent path variable, X is the independent path variable, c0 ... cn are the polynomial coefficients and n is the order of the polynomial. Because the path is defines as: P (bar) = 13.33 T(K) – 5306.67, the order of the polynomial (n) is 1 and c0 = -5306.67, C1 = 13.33

```
Enter n (<5)
1
Enter c( 0)
-5306.67
Enter c( 1)
13.33

Enter minimum and maximum values, respectively, for: T(K)
903
1273
```

For phase fractionation calculations the number of points computed along the path is determined by the 1d_path parameter. The values for this parameter are currently set to 40 and 160 points for the exploratory and autorefine cycles.

```
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 SiO2 K2O   CaO   FeO   H2O
for the bulk composition of interest:
0.57
3.64
8.95
70.09
2.87
0.28
6.93
6.66

Output a print file (Y/N)?
y

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
clinohumite models:      TiCh(PL)   Chum
…
For details on these models 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:
Ex14
```

(2) Doing the calculation (VERTEX)

Run VERTEX to make the calculation:

```
C:\PERPLEX\Perplex7110>vertex

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Enter the project name (the name assigned in BUILD) [default = my_project]:
ex14
…
-------------------------------------------------------------------------------
** Starting exploratory computational stage **
Choose computational mode:
    0 - no fractionation [default]
    1 - fractionate specified phases
    2 - fractionate all phases other than liquid
1

Enter the name of a phase to be fractionated
(left justified, <cr> to finish):
melt(W)

Enter the name of a phase to be fractionated
(left justified, <cr> to finish):
[enter]

The fractionated bulk composition will be written to file: fractionated_bulk.dat
The fractionated amount and composition of melt(W) will be written to file: ex14_melt(W).dat
```

Two output files will be created, summarizing (i) the new bulk composition after each episode of melt fractionation, and (ii) the amount and composition of fractionated melt.

```
At T(K)   = 903.000    P(bar)  = 6730.32
melt(W)    is not stable.
…
…
At T(K)   = 940.949    P(bar)  = 7236.18
melt(W)    is not stable.
```

Along the first part of the path, melt is not stable.

```
At T(K)   = 950.436    P(bar)  = 7362.64
melt(W)    is stable, but its mass fraction (0.006) is below or at the upper fractionation threshold (0.060).
```

At this point, melt is stable, but its amount is lower than the specified threshold and therefore it is not fractionated.

```
…
…
At T(K)   = 997.872    P(bar)  = 7994.96
melt(W)    is stable, but its mass fraction (0.059) is below or at the upper fractionation threshold (0.060).
```

```
At T(K)   = 1007.36    P(bar)  = 8121.43
current molar bulk composition is:
 0.570000     3.64000     8.95000     70.0900     2.87000     0.280000     6.93000     6.66000
fractionating  4.42227     moles of melt(W)   ; will change bulk by:
 0.304850    0.722404E-02 0.678565     5.61243     0.283407     0.288551E-01 0.184178E-01  2.68436
```

At this point, the melt amount exceeds the threshold and it is therefore removed from the system. The bulk composition is changed accordingly; the new bulk composition is used in the following calculation.

```
At T(K)   = 1016.85    P(bar)  = 8247.89
melt(W)    is stable, but its mass fraction (0.019) is below or at the upper fractionation threshold (0.060).

At T(K)   = 1026.33    P(bar)  = 8374.35
melt(W)    is stable, but its mass fraction (0.036) is below or at the upper fractionation threshold (0.060).

At T(K)   = 1035.82    P(bar)  = 8500.82
current molar bulk composition is:
 0.283946     3.63322     8.31327     64.8236     2.60407     0.252924     6.91272     4.14115
fractionating  4.54009     moles of melt(W)   ; will change bulk by:
 0.140250    0.933922E-02 0.703426     6.15715     0.446845     0.325444E-01 0.216507E-01  2.65569
```

At this point, the melt amount exceeds again the threshold and it is therefore removed from the system. The bulk composition is changed accordingly; the new bulk composition is used in the following calculation.

```
At T(K)   = 1045.31    P(bar)  = 8627.28
melt(W)    is stable, but its mass fraction (0.045) is below or at the upper fractionation threshold (0.060).

At T(K)   = 1054.79    P(bar)  = 8753.75
current molar bulk composition is:
 0.151091     3.62437     7.64694     58.9911     2.18078     0.222096     6.89221     1.62548
fractionating  2.58693     moles of melt(W)   ; will change bulk by:
 0.484346E-01 0.664976E-02 0.414454     3.68131     0.296387     0.178411E-01 0.136743E-01  1.46330
```

At this point, the melt amount exceeds again the threshold and it is therefore removed from the system. The bulk composition is changed accordingly; the new bulk composition is used in the following calculation.

```
At T(K)   = 1045.31    P(bar)  = 8627.28
melt(W)    is stable, but its mass fraction (0.045) is below or at the upper fractionation threshold (0.060).

At T(K)   = 1054.79    P(bar)  = 8753.75
current molar bulk composition is:
  1.61569     3.62436     7.64446     58.9616     2.17871     0.222055     6.89218     0.150902
fractionating  2.57132     moles of melt(W)   ; will change bulk by:
  1.45417    0.660220E-02 0.411835     3.66056     0.294591     0.176953E-01 0.135731E-01 0.481436E-01
```

At this point, the melt amount exceeds again the threshold and it is therefore removed from the system. The bulk composition is changed accordingly; the new bulk composition is used in the following calculation.

```
At T(K)   = 1064.28    P(bar)  = 8880.21
melt(W)    is stable, but its mass fraction (0.013) is below or at the upper fractionation threshold (0.060)
…
…
At T(K)   = 1273.00    P(bar)  = 11662.4
melt(W)    is stable, but its mass fraction (0.034) is below or at the upper fractionation threshold (0.060).
--------------------------------------------------------------------------------
```

```
Exploratory stage generated:
     27 compositions for: feldspar
     18 compositions for: Gt(W)
     41 compositions for: melt(W)
     21 compositions for: Mica(W)
      2 compositions for: St(W)
      2 compositions for: Opx(W)
     17 compositions for: Bi(W)
      2 compositions for: Crd(W)
Total number of compositions:     130
--------------------------------------------------------------------------------
--------------------------------------------------------------------------------
** Starting auto-refine computational stage **
The fractionated bulk composition will be written to file: fractionated_bulk.dat
The fractionated amount and composition of melt(W) will be written to file: ex14_melt(W).dat

At T(K)    = 903.000     P(bar)  = 6730.32
melt(W)    is not stable.
…
…
At T(K)    = 949.541     P(bar)  = 7350.71
melt(W)    is not stable.

At T(K)    = 951.868     P(bar)  = 7381.73
melt(W)    is stable, but its mass fraction (0.014) is below or at the upper fractionation threshold (0.060).
…
…
At T(K)    = 996.082     P(bar)  = 7971.10
melt(W)    is stable, but its mass fraction (0.053) is below or at the upper fractionation threshold (0.060).

At T(K)    = 998.409     P(bar)  = 8002.12
current molar bulk composition is:
 0.570000      3.64000      8.95000      70.0900      2.87000     0.280000      6.93000      6.66000
fractionating  3.36189     moles of melt(W)   ; will change bulk by:
 0.249703     0.496607E-02 0.508181      4.19645      0.197935     0.197173E-01 0.138946E-01  2.06143

At T(K)    = 1000.74     P(bar)  = 8033.14
melt(W)    is stable, but its mass fraction (0.012) is below or at the upper fractionation threshold (0.060).
…
…
At T(K)    = 1026.33     P(bar)  = 8374.35
melt(W)    is stable, but its mass fraction (0.058) is below or at the upper fractionation threshold (0.060).

At T(K)    = 1028.66     P(bar)  = 8405.37
current molar bulk composition is:
 0.340834     3.63544      8.48361      66.2387      2.68834     0.261904      6.91725      4.76811
fractionating  3.46279     moles of melt(W)   ; will change bulk by:
 0.154197     0.682296E-02 0.537822      4.59919      0.297693     0.245841E-01 0.156999E-01  2.04894

At T(K)    = 1030.99     P(bar)  = 8436.39
melt(W)    is stable, but its mass fraction (0.014) is below or at the upper fractionation threshold (0.060).
…
```

```
…
At T(K)    = 1034.61     P(bar)  = 8484.69
melt(W)    is stable, but its mass fraction (0.028) is below or at the upper fractionation threshold (0.060).
…
…
At T(K)    = 1040.30     P(bar)  = 8560.47
current molar bulk composition is:
 0.197704      3.62911      7.98439      61.9696      2.41202      0.239085      6.90268      2.86623
fractionating  3.71566      moles of melt(W)   ; will change bulk by:
 0.841463E-01 0.783010E-02 0.576621      5.11261      0.395649      0.268050E-01 0.181919E-01  2.15469

At T(K)    = 1042.62     P(bar)  = 8591.49
melt(W)    is stable, but its mass fraction (0.009) is below or at the upper fractionation threshold (0.060).
…
…
At T(K)    = 1172.94     P(bar)  = 10328.6
melt(W)    is stable, but its mass fraction (0.060) is below or at the upper fractionation threshold (0.060).

At T(K)    = 1175.26     P(bar)  = 10359.6
current molar bulk composition is:
 0.118680      3.62176      7.44288      57.1682      2.04046      0.213912      6.88559      0.842711
fractionating  1.93207      moles of melt(W)   ; will change bulk by:
 0.270879E-01 0.951955E-02 0.424319      3.52139      0.312836      0.223120E-01 0.273824E-01 0.842711

At T(K)    = 1177.59     P(bar)  = 10390.6
melt(W)    is stable, but its mass fraction (0.005) is below or at the upper fractionation threshold (0.060)….
…
At T(K)    = 1273.00     P(bar)  = 11662.4
melt(W)    is stable, but its mass fraction (0.009) is below or at the upper fractionation threshold (0.060).
--------------------------------------------------------------------------------
    Timing                  min.         % of total
  Static G calculation        0.0000            0.0
  Dynamic G calculation       0.27865E-01       30.7
  Static LP                   0.0000            0.0
  Dynamic LP                  0.18750E-01       20.7
  Successive QP               0.38802E-01       42.8
  Total of above              0.85417E-01       94.3
  Total elapsed time          0.90625E-01       100.0
--------------------------------------------------------------------------------
End of job: ex14
--------------------------------------------------------------------------------
```

(3) Calculating cumulative modes for the melt-fractionated system (WERAMI)

Run WERAMI to calculate the variation in the MODES of ALL the phases along the investigated path.

```
C:\PERPLEX\Perplex7110>werami

Perple_X release 7.1.10 Dec 21, 2024.
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```

```
Enter the project name (the name assigned in BUILD) [default = my_project]:
ex14

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] 0-150
  aq_solvent_composition  y       [y] m: y => mol fraction, m => molality
  aq_solute_composition   m       y [m]: y => mol fraction, m => molality
  spreadsheet           T       [T] F
  logarithmic_p         F       [F] T
  logarithmic_X         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         T       [T] F
  solution_names        abb     [model] abbreviation full
  structural_formulae    T       [T] F
  output_species        T       [T] F
  output_species_props   F       [F] T
  seismic_output        som     [some] none all
  poisson_test          F       [F] T
  interim_results       aut     [auto] off manual
  sample_on_grid        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
  finite_strain_alpha    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      [2] >0
  finite_difference_p    1.0E+04  [1d4] >0; fraction = 1.0E-03  [1d-3]
 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
  fluid_shear_modulus     T        [T] F
  phi_d                   0.36     [0.36] 0->1
 Error/warning control options:
  pause_on_error          T        [T] F
  max_warn_limit          5        [5]
  warn_interactive        T        [T] F
  aq_error_ver100         F        [F] T, abort during iteration
  aq_error_ver101         T        [T] F, solute undersaturation abort
  aq_error_ver102         T        [T] F, pure + impure solvent abort
  aq_error_ver103         T        [T] F, out-of-range HKF g abort
  aq_error_ver104         T        [T] F, abort on failed respeciation
  warning_ver637          T        [T] F
  error_ver109            T        [T] F
  do_not_reset_options    F        [F] T, prevents automatic resets
To change these options see: www.perplex.ethz.ch/perplex_options.html

--------------------------------------------------------------------------------
Select operational mode:
    1 - properties at specified conditions
    3 - properties along the 1d computational path
    0 - EXIT
3

Select a property:
   1 - Specific Enthalpy (J/m3)
   2 - Density (kg/m3)
   3 - Specific heat capacity (J/K/m3)
   4 - Expansivity (1/K, for volume)
   5 - Compressibility (1/bar, for volume)
   6 - 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

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

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

Change default variable range (y/n)?
n

**warning ver178** at T(K)=   903.0     P(bar)=   6730.
the shear modulus of: Bio
is missing or invalid and has been estimated with the poisson_ratio option
…
…

Data ranges excluding values equal to bad_number (       NaN) specified in perplex_option.dat:
    Bio          Mica         Gt           Fsp          Fsp          q            H2O          Melt         sill
min    0.178637        4.64365        5.82289       0.377491       0.560083        40.3374        0.272659        0.689861
0.229425
max    18.3914       23.9685       25.6439       24.6676       7.78750       48.4719       0.507922       10.6985       5.82666

Output has been written to two files:
    plt format is in file: ex14_1.plt
    1d tab format is in file: ex14_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
```

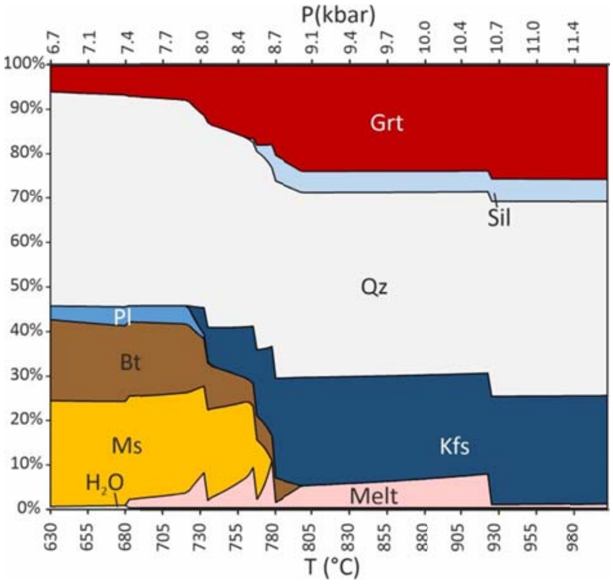
```
for details on tab format refer to:     perplex.ethz.ch/perplex/faq/Perple_X_tab_file_format.txt

Select operational mode:
   1 - properties at specified conditions
   3 - properties along the 1d computational path
   0 - EXIT
0
```

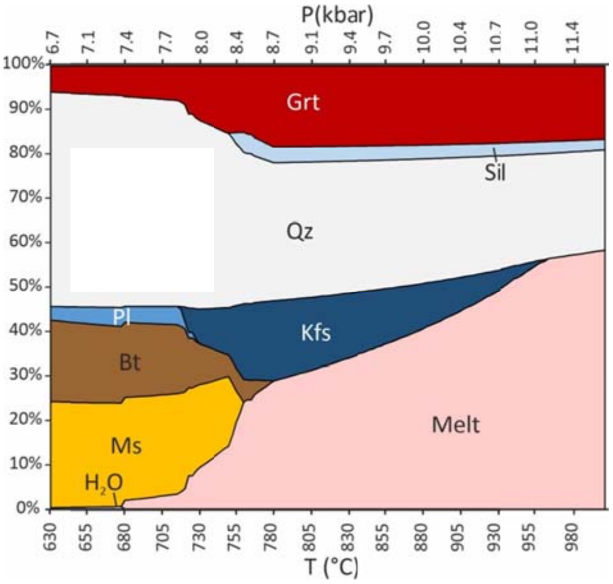
At the end, you have a new file (ex14_1.tab) in the Perple_X folder.

You can open the ex14_1.tab file using EXCEL; replace the NaN values with 0 and plot the data using the option Area Graph (see Ex. 10 and Ex.13).

MELT-FRACTIONATED SCENARIO



UNFRACTIONATED SCENARIO



The obtained results are coherent with natural and experimental observations, which suggest that melt extraction generally occurs when a critical threshold of 7-10 vol% of melt is reached in the source rock.

Ex 15

Ex. 15 – INDIRECT modelling of an anatectic METAPELITE

In Ex. 13 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** (see also Ex. 14)**.**

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 generally 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)**, <u>but may not be valid for the prograde evolution of the rock</u>.

(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**.

For a more comprehensive discussion on the melt-reintegration approach, refer to:

Bartoli (2017). Phase equilibria modelling of residual migmatites and granulites: An evaluation of the melt-reintegration approach. J. Metamorph Geol., 35, 919–942

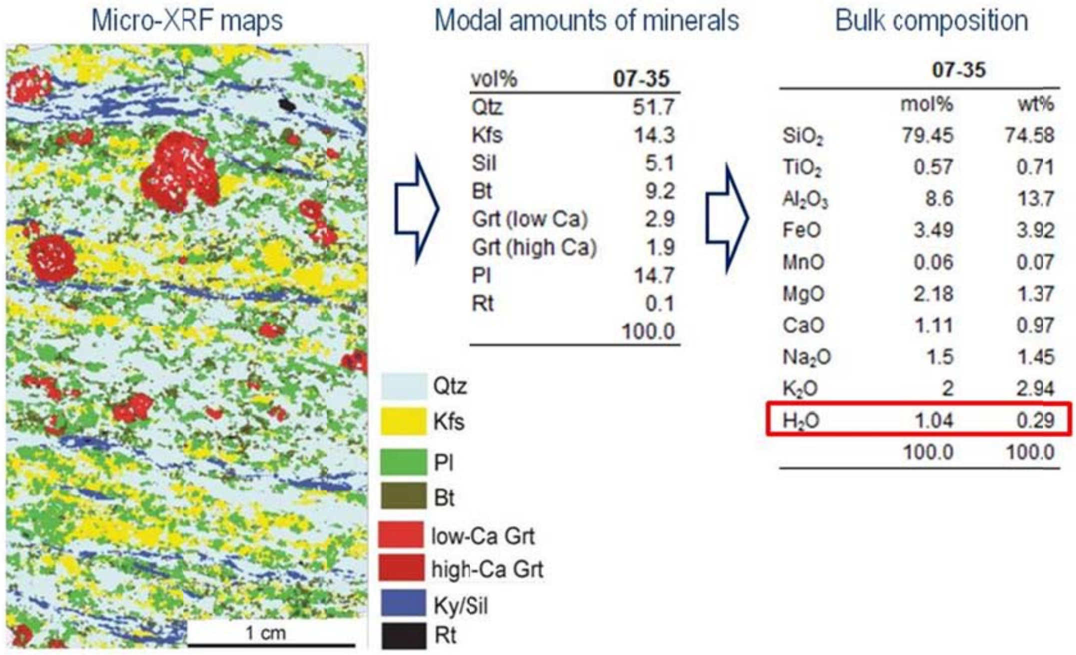
Ex. 15.1 – P-T EVOLUTION from PEAK conditions to FINAL MELT CRYSTALLIZATION

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, unless your sample is very fresh!)**.

My suggested method is to combine the mineral proportions obtained from the modal estimate of an X-ray 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%):

SiO2=79.45; TiO2=0.57; Al2O3=8.6, FeO=3.49, MgO=2.18, CaO=1.11, Na2O=1.5, K2O=2.00, H2O=1.04

T=700-900°C

P=3-15 kbar

Because the problem is similar to that of Ex. 13, we can try to skip the BUILD session and to directly edit the input file, starting from that of Ex. 13.

NB: Add TiO2 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\Perplex7110>vertex

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Enter the project name (the name assigned in BUILD) [default = my_project]:
ex15
…
```

(3) Plotting the calculated phase diagram (PSSECT)

Run PSSECT to plot the calculated pseudosection:

```
C:\PERPLEX\Perplex7110>pssect

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Copyright (C) 1986-2024 James A D Connolly <www.perplex.ethz.ch/copyright.html>.

Enter the project name (the name assigned in BUILD) [default = my_project]:
ex15
…
```
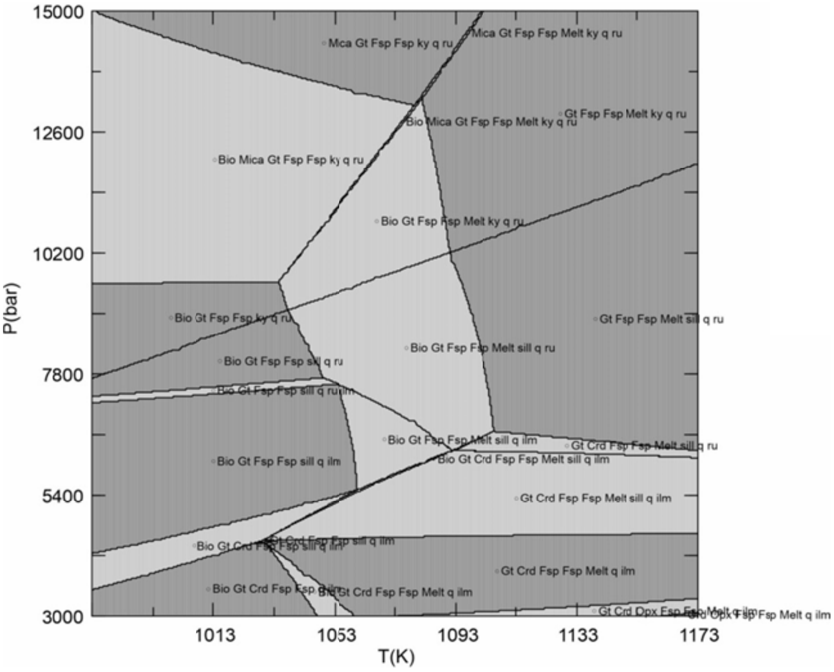



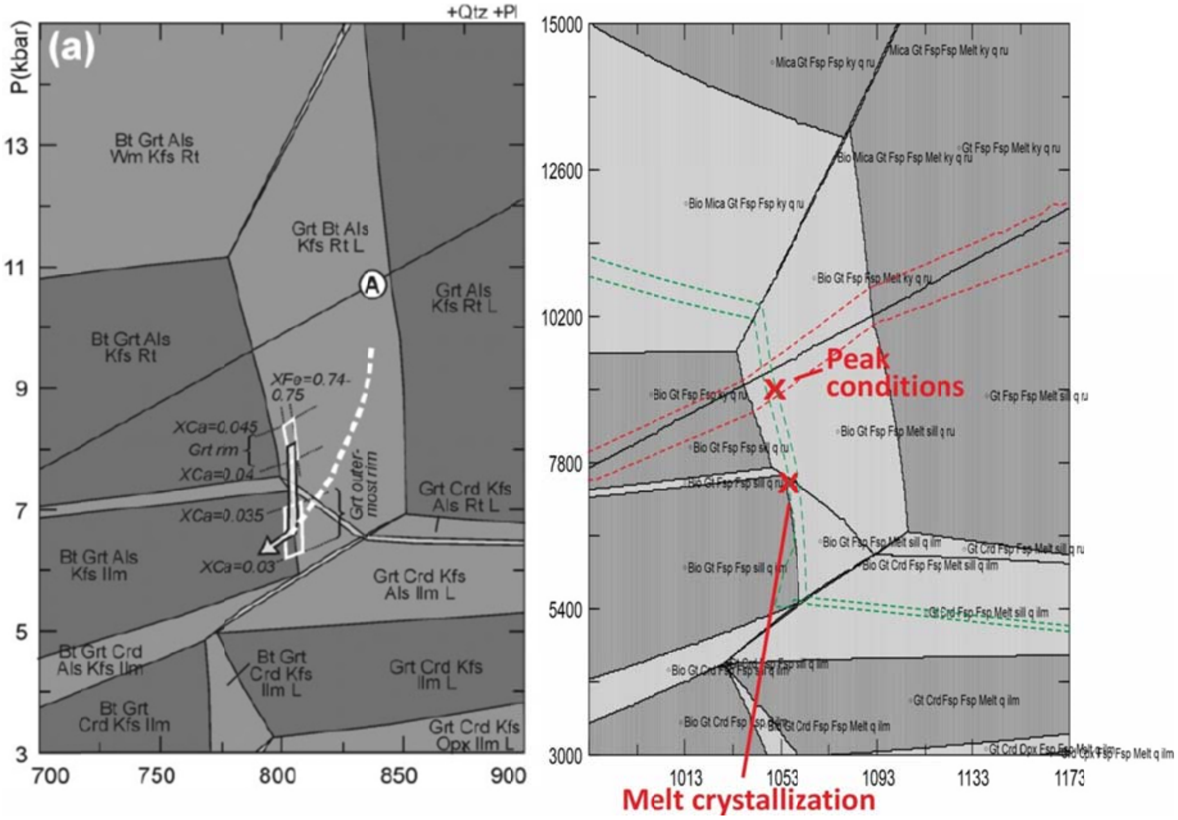
Peak P-T conditions can be derived by:

(a) the stability field of the peak assemblage (Grt + Bt + Kfs + Pl + Sil + Qz + Rt + L);

(b) the modelled vs. observed garnet composition (see details in Groppo et al., 2012)

P-T conditions of final melt crystallization are given by:

(a) the intersection between the MODELLED ISOMODES of each phase and the *solidus*, that should correspond to the MEASURED mineral modes.



Comparison with Fig. 10a in Groppo et al. (2012). Minor differences in the topology of the two diagrams are due to the different thermodynamic databases and solid solution models used.

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: 780°C, 7.5 kbar) are comparable (within the error) with the observed mineral modes.

Werami, option 1

```
Stable phases at:
                              T(K)     =  1053.00
                              P(bar)   =  7500.00

Phase Compositions (molar  proportions):
                    wt %     vol %    mol %     mol      Na2O    MgO      Al2O3   SiO2     K2O      CaO      FeO      TiO2     H2O
Bio            9.40     8.44     2.05     1.30     0.00000  1.27809  0.78267  2.71733  0.50000  0.00000  1.23685  0.20239  0.79761
Gt             5.31     3.56     1.13     0.717    0.00000  0.71599  1.00000  3.00000  0.00000  0.09329  2.19072  0.00000  0.00000
Fsp            14.55    15.06    5.46     3.47     0.32145  0.00000  0.63863  2.72274  0.03992  0.27726  0.00000  0.00000  0.00000
Fsp            14.02    14.94    5.13     3.27     0.11746  0.00000  0.51228  2.97545  0.37027  0.02455  0.00000  0.00000  0.00000
sill           7.53     6.32     4.67     2.97     0.00000  0.00000  1.00000  1.00000  0.00000  0.00000  0.00000  0.00000  0.00000
q              48.47    51.26    81.09    51.6     0.00000  0.00000  0.00000  1.00000  0.00000  0.00000  0.00000  0.00000  0.00000
ilm            0.73     0.42     0.48     0.306    0.00000  0.00000  0.00000  0.00000  0.00000  0.00000  1.00000  1.00000  0.00000
```

Mineral modes

	780°C, 7.5 kbar	
	observed	modelled
Qtz	51.7	51.2
Kfs	14.3	14.9
Sil	5.1	6.3
Bt	9.2	8.4
Grt	4.8	3.6
Pl	14.7	15.0

Ex. 15.2 – 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. 5% of melt); 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 the intersection between the solidus and the presumed prograde P–T path 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** (770°C, 9.0 kbar)

```
Stable phases at:
                 T(K)    =  1043.00
                 P(bar)  =  9000.00

Phase Compositions (molar  proportions):
            wt %    vol %   mol %    mol      Na2O    MgO      Al2O3    SiO2     K2O      CaO      FeO      TiO2     H2O
Bio         8.37    7.57    1.84    1.16    0.00000  1.30195  0.78636  2.71364  0.50000  0.00000  1.22075  0.19093  0.80907
Gt          7.04    4.75    1.50    0.951   0.00000  0.69931  1.00000  3.00000  0.00000  0.12451  2.17618  0.00000  0.00000
Fsp        14.25   14.84    5.38    3.40    0.32671  0.00000  0.63419  2.73162  0.03910  0.26838  0.00000  0.00000  0.00000
Fsp        14.49   15.52    5.33    3.37    0.11134  0.00000  0.51126  2.97748  0.37739  0.02252  0.00000  0.00000  0.00000
Melt        0.32    0.40    0.27    0.170   0.07069  0.00170  0.16918  1.34351  0.06967  0.01110  0.00515  0.00000  0.58089
sill        7.15    6.04    4.46    2.82    0.00000  0.00000  1.00000  1.00000  0.00000  0.00000  0.00000  0.00000  0.00000
q          47.94   50.59   80.67   51.0     0.00000  0.00000  0.00000  1.00000  0.00000  0.00000  0.00000  0.00000  0.00000
ru          0.43    0.28    0.55    0.348   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.

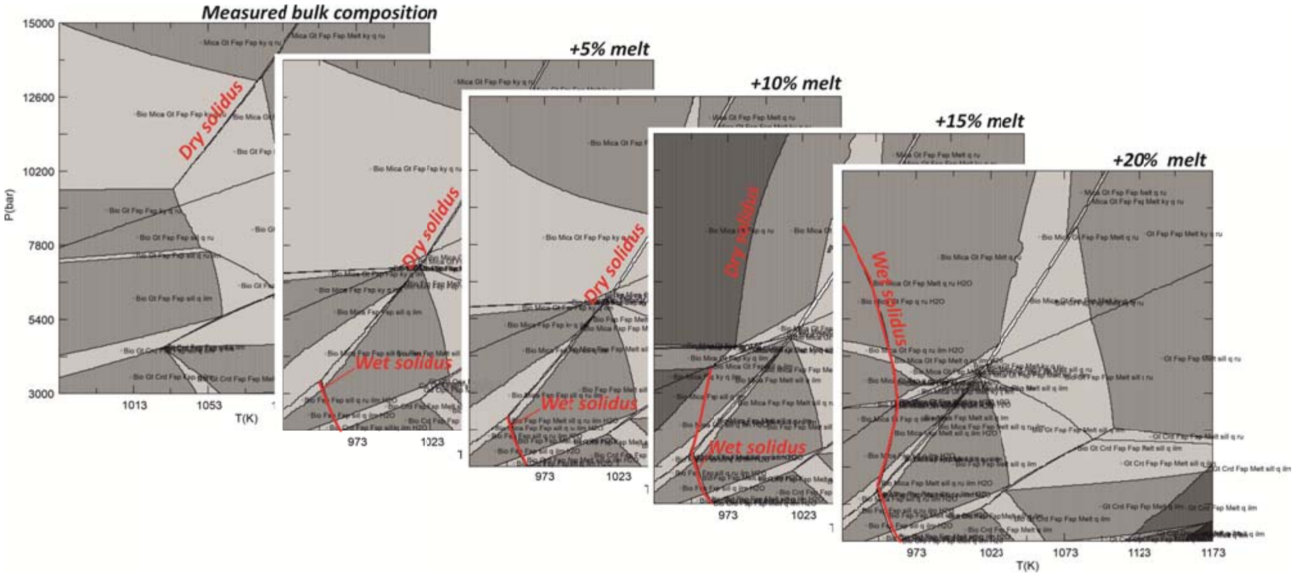
	melt composition (770°C, 9.0 kbar)		BC**	Melt reintegrated bulk compositions							
	mol*	mol%	mol%	+ 0.05 mol%		+ 0.10 mol%		+ 0.15 mol%		+ 0.20 mol%	
SiO2	1.3435	59.66	79.45	82.4	78.55	85.4	77.69	88.4	76.91	91.4	76.19
TiO2	0.0000	0.00	0.57	0.6	0.54	0.6	0.52	0.6	0.50	0.6	0.48
Al2O3	0.1692	7.51	8.60	9.0	8.55	9.4	8.51	9.7	8.46	10.1	8.42
FeO	0.0052	0.23	3.49	3.5	3.34	3.5	3.20	3.5	3.07	3.5	2.95
MgO	0.0017	0.08	2.18	2.2	2.08	2.2	1.99	2.2	1.91	2.2	1.83
CaO	0.0111	0.49	1.11	1.1	1.08	1.2	1.05	1.2	1.03	1.2	1.01
Na2O	0.0707	3.14	1.50	1.7	1.58	1.8	1.65	2.0	1.71	2.1	1.77
K2O	0.0697	3.09	2.00	2.2	2.05	2.3	2.10	2.5	2.14	2.6	2.18
H2O	0.5809	25.80	1.04	2.3	2.22	3.6	3.29	4.9	4.27	6.2	5.17
Total	2.2519	100.00	99.94	104.9	100.00	109.9	100.00	114.9	100.00	119.9	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 (+5% melt); 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 20% 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).