PERPLE_X TUTORIALS

This set of 14 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 7.1.5** (released on December 1, 2023). 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 14 exercises are as follows:

Understanding the differences between projections, chemographies and pseudosections

Working with solid solutions

Working with solid solutions in a more complex system

Modelling a melt-bearing system

Ex 1

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

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

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

(1) Definition of the problem (BUILD)

C:\PERPLEX\Perplex715>build

Perple_X release 7.1.5, Dec 1, 2023.
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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 = hp02ver.dat]:
The HP (Holland & Powell) databases are the most used in metamorphic petrology. In this exercise we will use the hp02 (Holland & Powell, 1998, revised 2002). We will then compare the results with that obtained using the more recent hp62 database (from the THERMOCALC version TC-DS62; Holland & Powell, 2011). More information about the HP databases are given at https://hpxeosandthermocalc.org/the-hpx-eos/
hp02ver.dat

Enter the computational option file name [default = perplex_option.dat]:
See: www.perplex.ethz.ch/perplex_options.html
Here you can press 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 Fe_2O_3 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 SiO_2 as a saturated component.

NB. If more than one saturated component is specified, Perple_X applies the constraints sequentially, e.g., if Al_2O_3 and SiO_2 are specified as the first and second components, then the excess phases might be corundum + andalusite, if the order is reversed then, at the same conditions, the stable phases would be quartz + andalusite. This sequence is referred to as the **saturation hierarchy**.

y

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

Select < 6 saturated components from the set:
 NA2O MGO AL2O3 SIO2 K2O CAO TIO2 MNO FEO NIO ZRO2 CL2 O2   H2O CO2
Enter names, 1 per line, press <enter> to finish:

SIO2
(NB. It is CASE-SENSITIVE!).

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

Select thermodynamic components from the set:
 NA2O MGO AL2O3 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\Perplex715>convex

Perple_X release 7.1.5, Dec 1, 2023.
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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:
 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
 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
 GFSM                 F        [F] T GFSM/special_component toggle
 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_ion_H+            T        [T] F => use OH-
 aq_oxide_components  F        [F] T
 aq_solvent_solvus    T        [T] F
 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\Perplex715>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
```
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

ky = sill

ky = and

and = sill

(1)
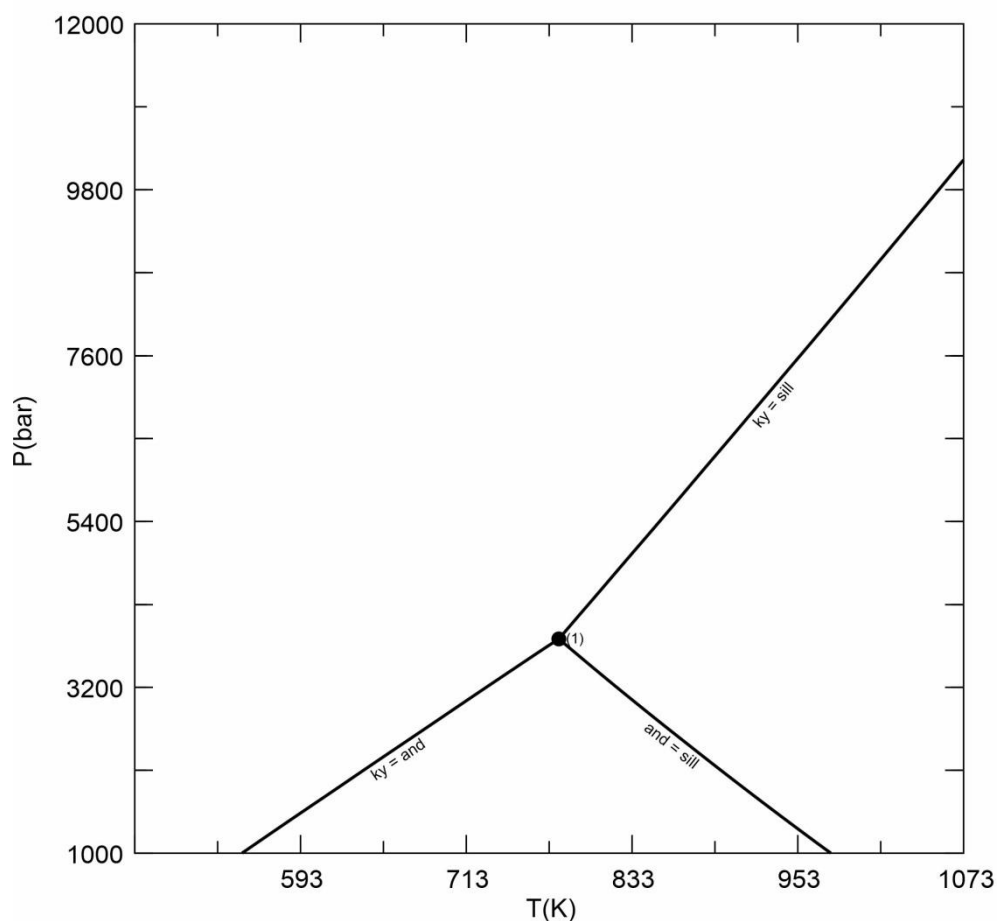
The alumino-silicate triple point is modelled at 507°C, 3.8 kbar.

(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\Perplex715>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
```
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.

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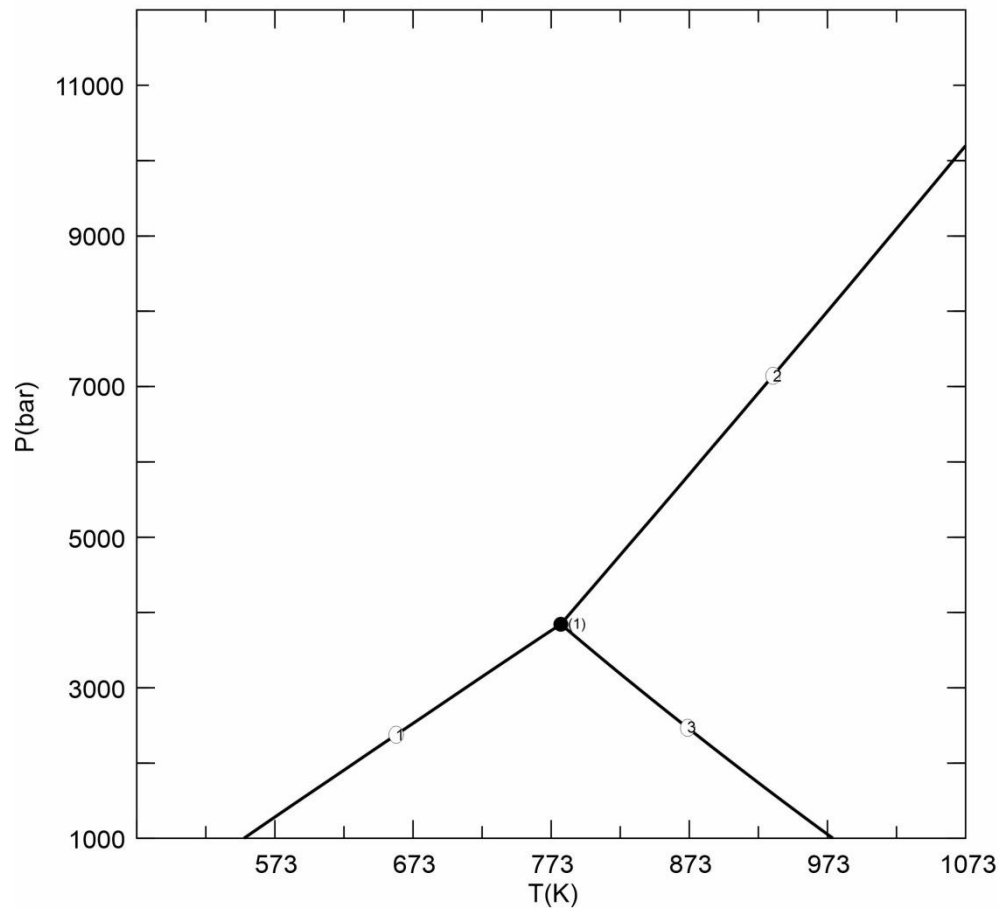
Equilibria corresponding to each reaction number are explained in the ex1.prn file.

(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
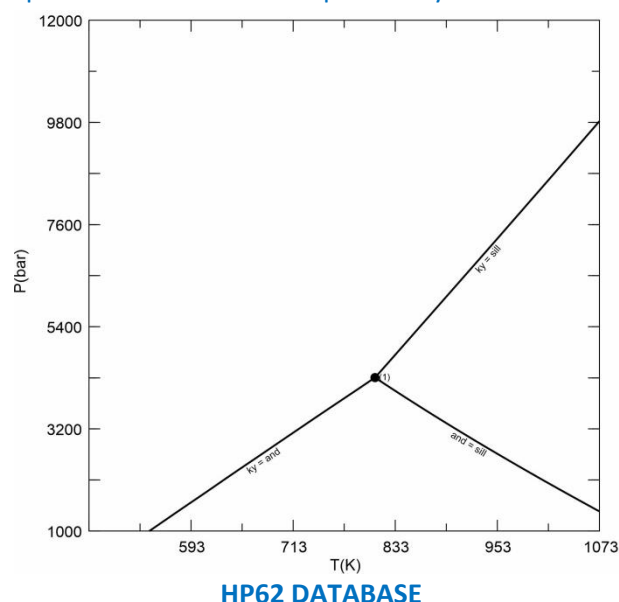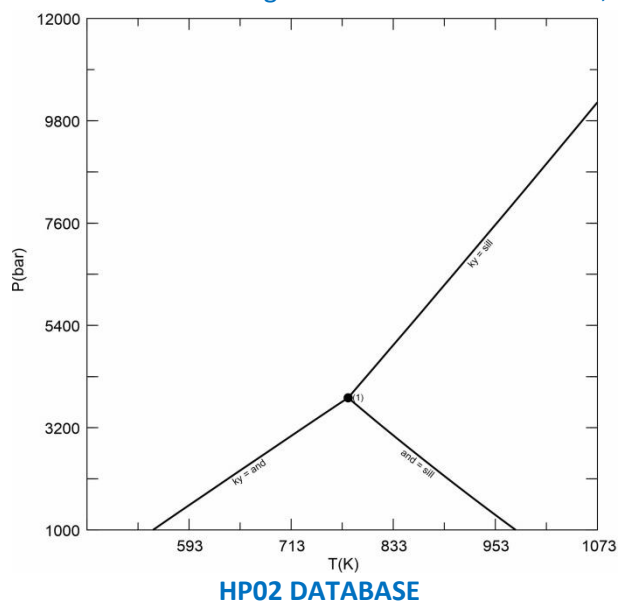
The alumino-silicate triple point is now modelled at 550°C, 4.4 kbar.
The change in the position of the triple point dates back to the 2004 revision of the HP database. In the 2002 version (hp02ver.dat) the aluminosilicate triple point is at 3.8 kbar and 507 °C, consistent with Holdaway's (1971) estimate; 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 (<u>no solid solutions</u>)

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

(1) Definition of the problem (BUILD)

C:\PERPLEX\Perplex715>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]:
ex2
The problem definition file will be named: ex2.dat

Enter thermodynamic data file name [default = hp02ver.dat]:
The HP (Holland & Powell) databases are the most used in metamorphic petrology. One of the most recent HP databases is hp62 from the THERMOCALC version TC-DS62; Holland & Powell, 2011). I suggest using the hp62ver.dat database, which has been tested in the last years and has demonstrated to be reliable for both metapelitic and metabasic systems.
hp62ver.dat

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

The current data base components are:
Na2O MgO Al2O3 SiO2 K2O CaO TiO2 MnO FeO NiO ZrO2 Cl2 O2 H2O CO2 CuO Cr2O3 S2 F2 N2 ZnO
Transform them (Y/N)?
n
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)?

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

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

Select thermodynamic components from the set:
Na2O MgO Al2O3 SiO2 K2O CaO TiO2 MnO FeO NiO ZrO2 Cl2 O2 CO2 CuO Cr2O3 S2 F2 N2 ZnO
Enter names, 1 per line, press <enter> to finish:
MgO
CaO
SiO2

Because the thermodynamic data file identifies: H2O as special components, you will be prompted next for the EoS to be used for the corresponding composants and mixtures thereof. To override this behavior, e.g., to use a generic hybrid fluid EoS (GFSM) either:
  set/add the GFSM option to T in your option file
  or delete the special_component section from the thermodynamic data file header.
NOTE: the EoS choice specified here will override the EoS choice specified by the hybrid_EoS option, tooverride this behavior delete the special_component section from the the thermodynamic data file header.

Select fluid equation of state:
  0 - X(CO2) H2O-CO2 Modified Redlich-Kwong (MRK) DeSantis et al 74
  1 - X(CO2) H2O-CO2 HSMRK Kerrick & Jacobs 81
  2 - X(CO2) H2O-CO2 MRK hybrid-EoS*
  5 - X(CO2) H2O-CO2 CORK Holland & Powell 91, 98
  8 - f(O2/CO2) C-buffered COH MRK hybrid-EoS*
  10 - X(O) C-buffered COH MRK hybrid-EoS Connolly & Cesare 93*
  12 - X(O)-f(S2) C-buffered COHS MRK hybrid-EoS Connolly & Cesare 93*
  13 - X(H2) H2O-H2 MRK hybrid-EoS*
  14 - X(CO2) H2O-CO2 Pitzer & Sterner 94; Holland & Powell mixing 03
  15 - X(H2) H2O-H2 low T MRK hybrid-EoS*
  16 - X(O) H-O MRK hybrid-EoS*
  17 - X(O)-f(S2) H-O-S MRK hybrid-EoS*
  19 - X(O)-X(S) C-buffered COHS MRK hybrid-EoS Connolly & Cesare 93*
  20 - X(O)-X(C) COHS MRK hybrid-EoS Connolly & Cesare 93*
  24 - f(O2/CO2)-N/C C-buffered COHN MRK hybrid-EoS*
  25 - X(CO2)-X(NaCl) H2O-CO2-NaCl Aranovich et al 10
  26 - X(O) O-Si MRK Connolly 16
  27 - X(O)-X(C) C-O-H MRK hybrid-EoS*
*Hybrid EoS use the following pure species EoS, to change these associations modify the hybrid_EoS keywords in the perplex_option file:
    H2O - PSEoS Pitzer & Sterner 1994
    CO2 - PSEoS Pitzer & Sterner 1994
    CH4 - 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 Ca3Si2O7
lrn		larnite Ca2SiO4
cstn		"Si-titanite" CaSi2O5 (one Si replaces Ti)
wo		wollastonite CaSiO3
pswo		pseudo-wollastonite CaSiO3
wal		wollastonite CaSiO3
ak		akermanite Ca2MgSi2O7
merw		merwinite Ca3MgSi2O8
mont		monticellite CaMgSiO4
chum		clinohumite Mg9Si4O16(OH)2
cen		clinoenstatite Mg2Si2O6
cumm		cummingtonite Mg7Si8O22(OH)2
cumm_dqf		cummingtonite for Diener et al. (2007) cAmph model
woL		wollastonite LIQUID
limL		lime LIQUID
mcpv		make definitions for Holland et al., 2013 mantle mineralogical model
cmpv		make definitions for Holland et al., 2013 mantle mineralogical model
cpv		make definitions for Holland et al., 2013 mantle mineralogical model

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

Include solution 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\Perplex715>convex

Perple_X release 7.1.5, Dec 1, 2023.
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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:

  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
  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
  GFSM   F   [F] T GFSM/special_component toggle
  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_ion_H+   T   [T] F => use OH-
  aq_oxide_components   F   [F] T
  aq_solvent_solvus   T   [T] F
  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   foTL   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\Perplex715>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
```

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\Perplex715>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
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
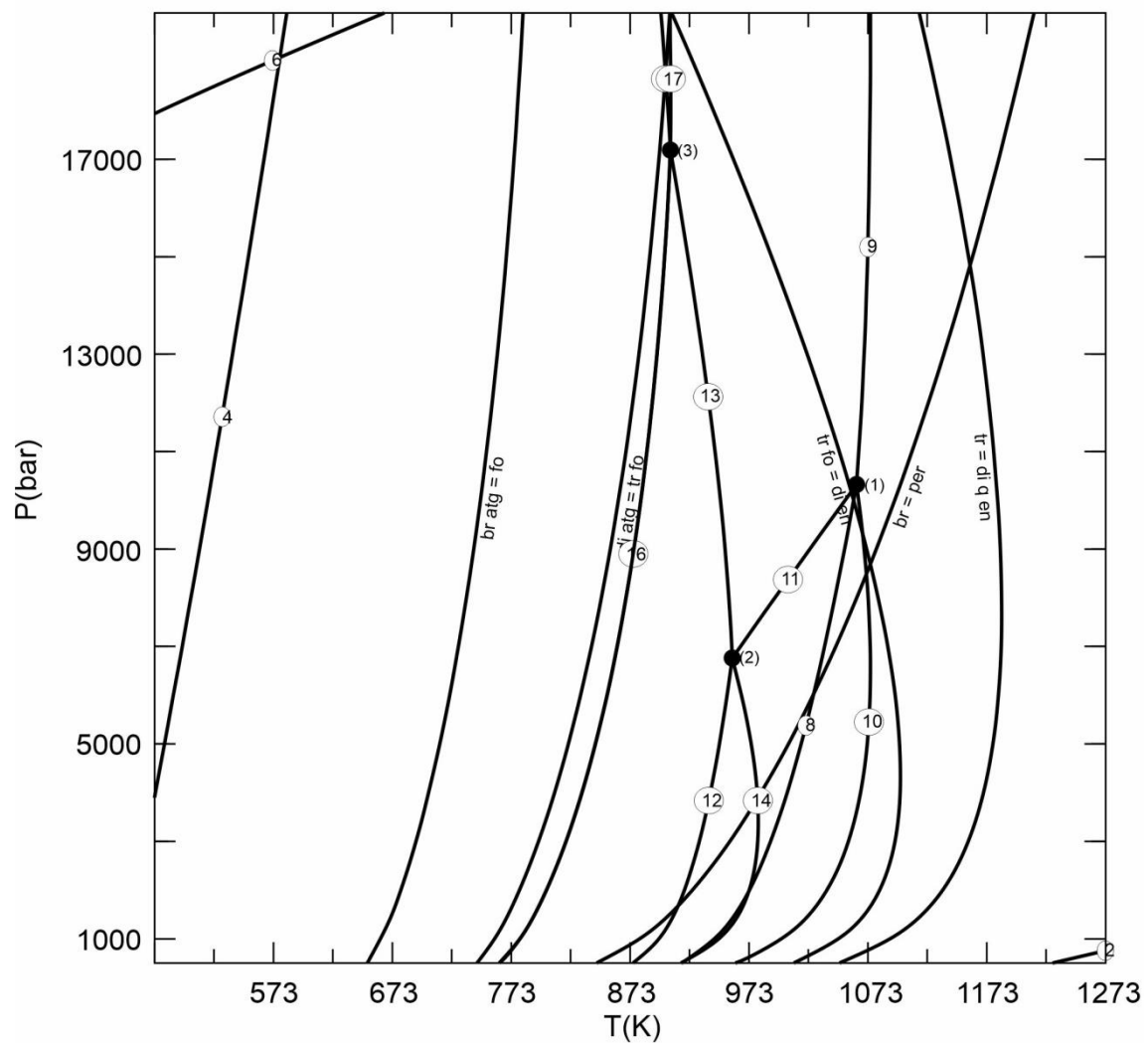
Equilibria corresponding to each reaction number are explained in the ex2.prn file.

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.
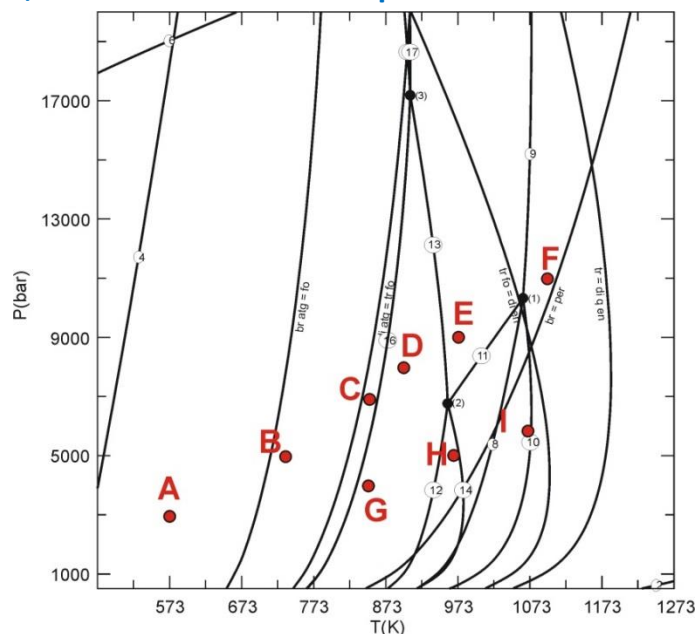
(1) Definition of the problem (BUILD)

C:\PERPLEX\Perplex715>build

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

Enter a name for this project (the name will be used as the root for all output file names) [default = my_project]:
ex3

The problem definition file will be named: ex3.dat

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

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

Reading 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.

Because the thermodynamic data file identifies: H2O as special components, you will be prompted next for the EoS to be used for the corresponding composants and mixtures thereof. To override this behavior, e.g., to use a generic hybrid fluid EoS (GFSM) either:
  set/add the GFSM option to T in your option file
  or delete the special_component section from the thermodynamic data file header.

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

Select fluid equation of state:
  0 - X(CO2) H2O-CO2 Modified Redlich-Kwong (MRK) DeSantis et al 74
  1 - X(CO2) H2O-CO2 HSMRK Kerrick & Jacobs 81
  2 - X(CO2) H2O-CO2 MRK hybrid-EoS*
  5 - X(CO2) H2O-CO2 CORK Holland & Powell 91, 98
  8 - f(O2/CO2) C-buffered COH MRK hybrid-EoS*
  10 - X(O) C-buffered COH MRK hybrid-EoS Connolly & Cesare 93*
  12 - X(O)-f(S2) C-buffered COHS MRK hybrid-EoS Connolly & Cesare 93*
  13 - X(H2) H2O-H2 MRK hybrid-EoS*
  14 - X(CO2) H2O-CO2 Pitzer & Sterner 94; Holland & Powell mixing 03
  15 - X(H2) H2O-H2 low T MRK hybrid-EoS*
  16 - X(O) H-O MRK hybrid-EoS*
  17 - X(O)-f(S2) H-O-S MRK hybrid-EoS*
  19 - X(O)-X(S) C-buffered COHS MRK hybrid-EoS Connolly & Cesare 93*
  20 - X(O)-X(C) COHS MRK hybrid-EoS Connolly & Cesare 93*
  24 - f(O2/CO2)-N/C C-buffered COHN MRK hybrid-EoS*
  25 - X(CO2)-X(NaCl) H2O-CO2-NaCl Aranovich et al 10
  26 - X(O) O-Si MRK Connolly 16
  27 - X(O)-X(C) C-O-H MRK hybrid-EoS*
*Hybrid EoS use the following pure species EoS, to change these associations modify the hybrid_EoS keywords in the perplex_option file:
    H2O - PSEoS Pitzer & Sterner 1994
    CO2 - PSEoS Pitzer & Sterner 1994
    CH4 - 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\Perplex715>convex

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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
  refinement_switch   F   [T] F
  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:
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
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
GFSM                 F        [F] T GFSM/special_component toggle
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_ion_H+            T        [T] F => use OH-
aq_oxide_components  F        [F] T
aq_solvent_solvus    T        [T] F
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   foTL   foHL   qHL

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

Computing the compositional phase relations at condition 2

cycle	1	1	1
cycle	2	2	3
cycle	3	4	5
cycle	4	6	7
cycle	5	8	8

Computing the compositional phase relations at condition 3

cycle	1	1	1
cycle	2	2	3
cycle	3	4	5
cycle	4	6	7
cycle	5	8	8

Computing the compositional phase relations at condition 4

cycle	1	1	1
cycle	2	2	3
cycle	3	4	5
cycle	4	6	7

Computing the compositional phase relations at condition 5

cycle	1	1	1
cycle	2	2	3
cycle	3	4	5
cycle	4	6	7
cycle	5	8	8

Computing the compositional phase relations at condition 6

cycle	1	1	1
cycle	2	2	3
cycle	3	4	5
cycle	4	6	7

Computing the compositional phase relations at condition 7

cycle	1	1	1
cycle	2	2	3
cycle	3	4	5
cycle	4	6	7

Computing the compositional phase relations at condition 8

cycle	1	1	1
cycle	2	2	3
cycle	3	4	5
cycle	4	6	7
cycle	5	8	8

Computing the compositional phase relations at condition 9

cycle	1	1	1
cycle	2	2	3
cycle	3	4	5
cycle	4	6	7
cycle	5	8	8

(3) Plotting the calculated phase diagram (PSVDRAW)

Run PSVDRAW to plot the calculated chemographies:

C:\PERPLEX\Perplex715>psvdraw

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Enter the project or plot file name [i.e., without the .plt suffix]:
ex3

Perple_X plot options are currently set as:
    Keyword: Value: Permitted values [default]:
    axis_label_scale   1.20   [1.2] (rel)
    bounding_box :
                0   [0] x-min (pts)
                0   [0] y-min (pts)
              800   [800] x-length (pts)
              800   [800] y-length (pts)
    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
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)

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

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

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

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

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

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

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

P(bar) =0.600E+04
T(K) =0.107E+04
Y(CO2) = 0.00
(fluid saturated)

Ex 4

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

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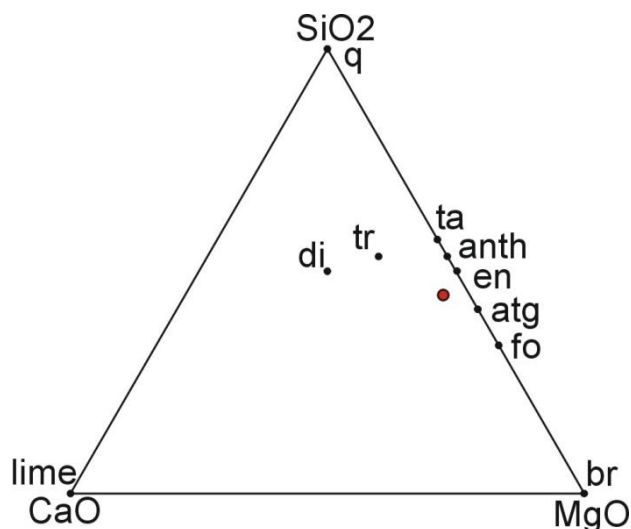
Combined with Ex. 2 and Ex. 3, this exercise is useful to understand the difference between P-T projections and P-T pseudosections.

(1) Definition of the problem (BUILD)

C:\PERPLEX\Perplex715>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 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 = hp02ver.dat]:
hp62ver.dat

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

Reading Perple_X options from: perplex_option.dat

The current data base components are:

Na2O MgO Al2O3 SiO2 K2O CaO TiO2 MnO   FeO NiO ZrO2 Cl2 O2 H2O CO2 CuO Cr2O3 S2 F2 N2 ZnO
Transform them (Y/N)?

n

Specify computational mode:
   1 - Convex-Hull minimization
   2 - Constrained minimization on a 2d grid [default]
   3 - Constrained minimization on a 1d grid
   4 - Output pseudocompound data
   5 - 1-d Phase fractionation
   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

Because the thermodynamic data file identifies: H2O as special components, you will be prompted next for the EoS to be used for the corresponding composants and mixtures thereof. To override this behavior, e.g., to use a generic hybrid fluid EoS (GFSM) either:
  set/add the GFSM option to T in your option file
  or delete the special_component section from the thermodynamic data file header.
NOTE: the EoS choice specified here will override the EoS choice specified by the hybrid_EoS option, tooverride this behavior delete the special_component section from the the thermodynamic data file header.

Select fluid equation of state:
   0 - X(CO2) H2O-CO2 Modified Redlich-Kwong (MRK) DeSantis et al 74
   1 - X(CO2) H2O-CO2 HSMRK Kerrick & Jacobs 81
   2 - X(CO2) H2O-CO2 MRK hybrid-EoS*
   5 - X(CO2) H2O-CO2 CORK Holland & Powell 91, 98
   8 - f(O2/CO2) C-buffered COH MRK hybrid-EoS*
   10 - X(O) C-buffered COH MRK hybrid-EoS Connolly & Cesare 93*
   12 - X(O)-f(S2) C-buffered COHS MRK hybrid-EoS Connolly & Cesare 93*
   13 - X(H2) H2O-H2 MRK hybrid-EoS*
   14 - X(CO2) H2O-CO2 Pitzer & Sterner 94; Holland & Powell mixing 03
   15 - X(H2) H2O-H2 low T MRK hybrid-EoS*
   16 - X(O) H-O MRK hybrid-EoS*
   17 - X(O)-f(S2) H-O-S MRK hybrid-EoS*
   19 - X(O)-X(S) C-buffered COHS MRK hybrid-EoS Connolly & Cesare 93*
   20 - X(O)-X(C) COHS MRK hybrid-EoS Connolly & Cesare 93*
   24 - f(O2/CO2)-N/C C-buffered COHN MRK hybrid-EoS*
   25 - X(CO2)-X(NaCl) H2O-CO2-NaCl Aranovich et al 10
   26 - X(O) O-Si MRK Connolly 16
   27 - X(O)-X(C) C-O-H MRK hybrid-EoS*
*Hybrid EoS use the following pure species EoS, to change these associations modify the hybrid_EoS keywords in the perplex_option file:
    H2O - PSEoS Pitzer & Sterner 1994
    CO2 - PSEoS Pitzer & Sterner 1994
    CH4 - 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	10	10	10 x 10 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\Perplex715>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
 refinement_switch   F   [T] F
 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   10 / 40 [10/40] >0, <2048; effective x-resolution   10 / 313 nodes
 y_nodes   10 / 40 [10/40] >0, <2048; effective y-resolution   10 / 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:
 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
 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
 GFSM   F   [F] T GFSM/special_component toggle
 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_ion_H+   T   [T] F => use OH-
 aq_oxide_components   F   [F] T
 aq_solvent_solvus   T   [T] F

```
   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   foTL   foHL   qHL
--------------------------------------------------------------------------------
**warning ver099**  no data for aqueous species, aq_output and aq_lagged_speciation disabled.

** Starting exploratory computational stage **
 2.5% done with low level grid.
 5.0% done with low level grid.
 7.5% done with low level grid.
 10.0% done with low level grid.
 12.5% done with low level grid.
 15.0% done with low level grid.
 17.5% done with low level grid.
 20.0% done with low level grid.
 22.5% done with low level grid.
 25.0% done with low level grid.
 27.5% done with low level grid.
 30.0% done with low level grid.
 32.5% done with low level grid.
 35.0% done with low level grid.
 37.5% done with low level grid.
```

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

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 **
  2.5% done with low level grid.
  5.0% done with low level grid.
  7.5% done with low level grid.
 10.0% done with low level grid.

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

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	0.26042E-03	2.7
Dynamic G calculation	0.0000	0.0
Static LP	0.26042E-03	2.7
Dynamic LP	0.0000	0.0
Successive QP	0.0000	0.0
Total of above	0.52083E-03	5.4
Total elapsed time	0.96354E-02	100.0

End of job: ex4

----

(3) Plotting the calculated phase diagram (PSSECT)

Run PSSECT to plot the calculated pseudosection:

C:\PERPLEX\Perplex715>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
```

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

PostScript will be written to file: ex4.ps
Modify the default plot (y/n)?
n
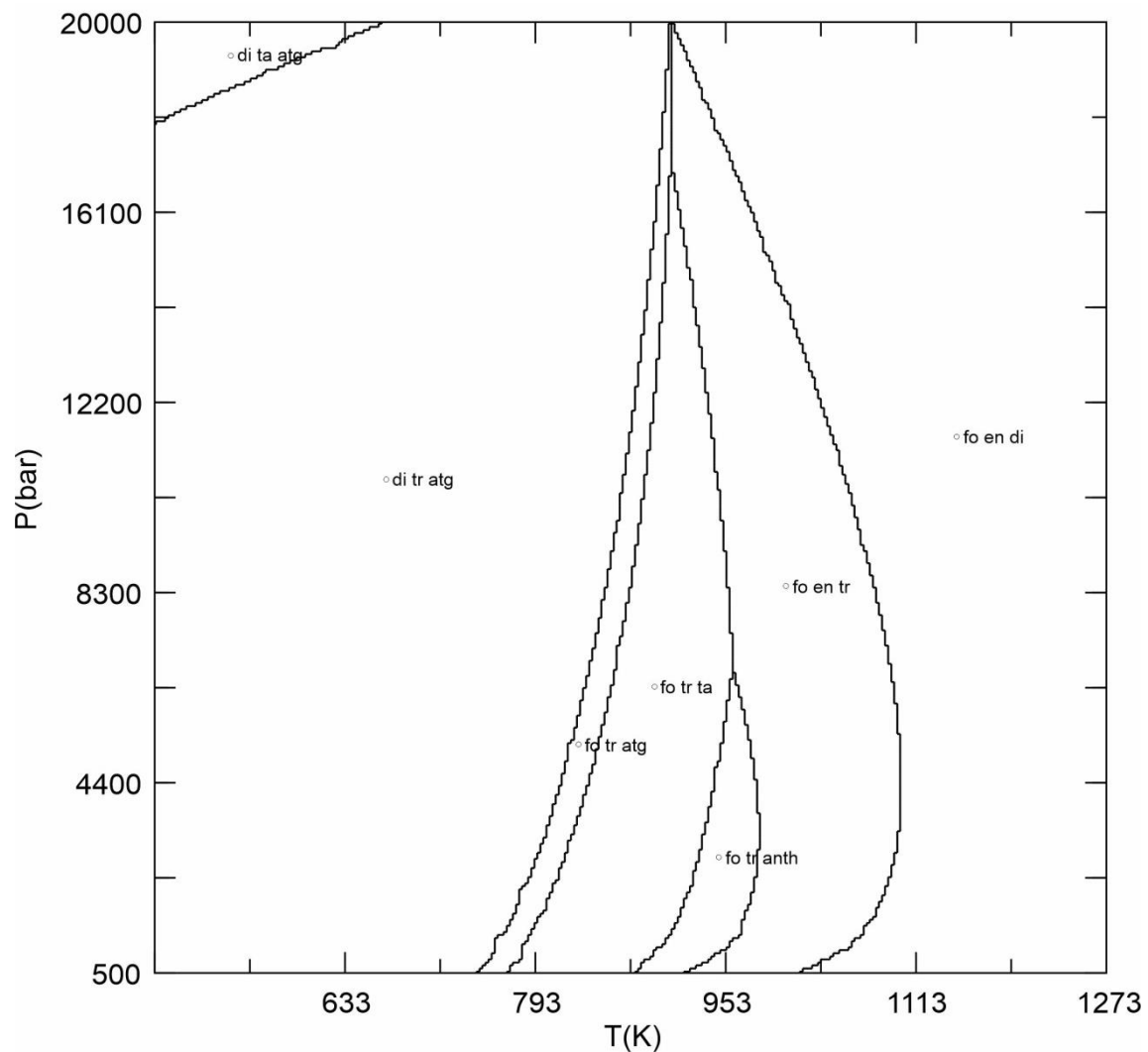
Being a very simple pseudosection (no solid solutions!), the stability fields of each mineral assemblage are separated by "real" reaction curves, i.e. UNIVARIANT CURVES, and all the field assemblages have the same variance. However, this is a very special case: pseudosections generally contain multi-variant field assemblages.
NB. The variance of each field is 2 [f= c-p+2; c=4 (CMSH); p=4 (remember that each field also contains H_2O)]

(4) Comparison between projection and pseudosection
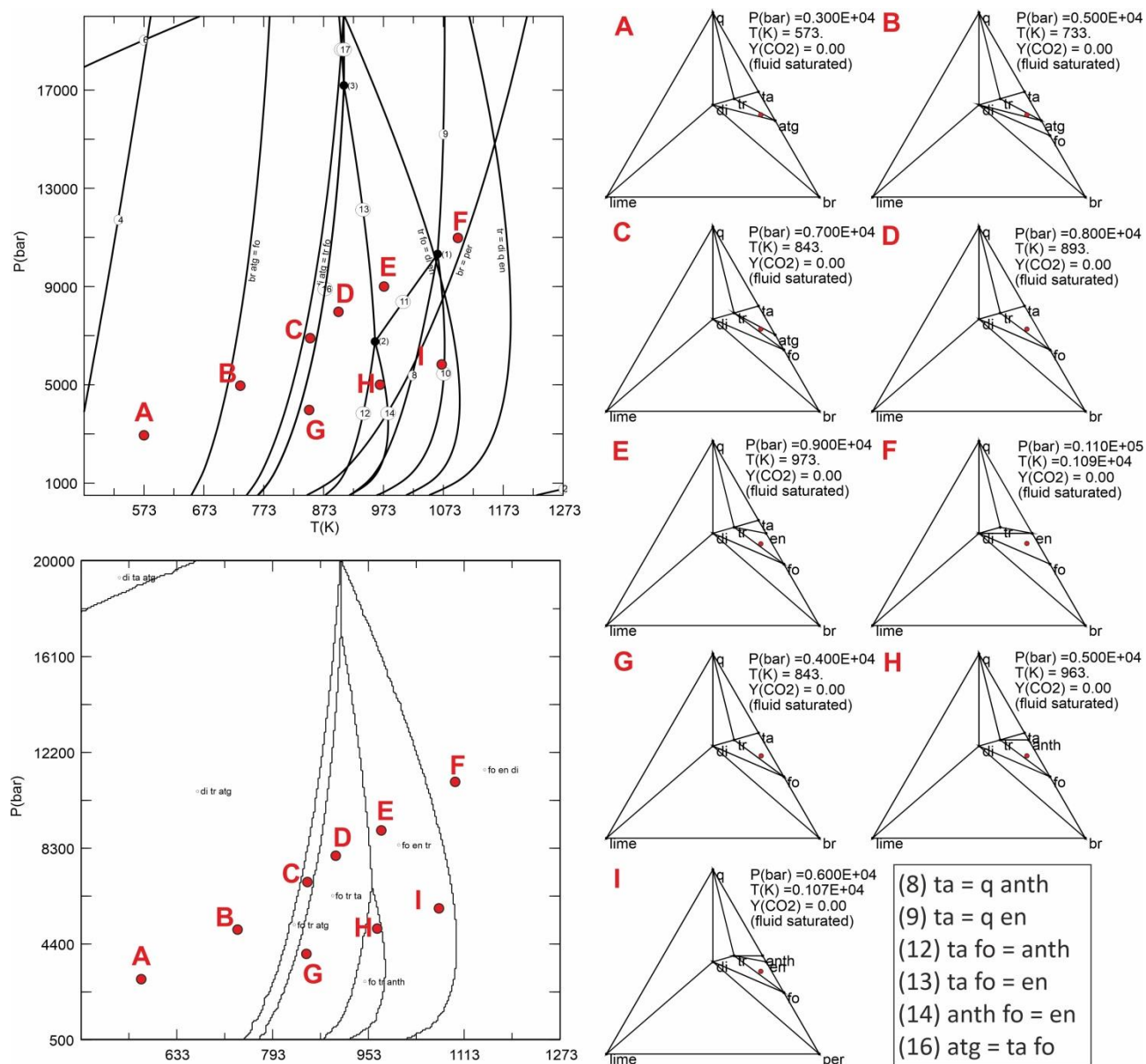
Comparison between the CMSH projection (Ex. 2) and the pseudosection (Ex. 4) calculated for a bulk composition MgO=50 mol%, SiO2=45 mol%, CaO=5 mol% (red dot in the chemographies – Ex. 3).
This specific bulk composition "sees" (i.e. is sensible to) only some of the reactions predicted by the P-T projection.

Ex 5

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

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(CO₂) projections and T-X(CO₂) pseudosections and allows you to become familiar with the use of H₂O-CO₂ fluids.

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

(1) Definition of the problem (BUILD)

C:\PERPLEX\Perplex715>build

Perple_X release 7.1.5, Dec 1, 2023.
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NO is the default (blank) answer to all Y/N prompts

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

The problem definition file will be named: ex5_1.dat

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

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

Reading 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

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

  set/add the GFSM option to T in your option file

  or delete the special_component section from the thermodynamic data file header.

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

Select fluid equation of state:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

    H2O - PSEoS Pitzer & Sterner 1994

    CO2 - PSEoS Pitzer & Sterner 1994

    CH4 - 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\Perplex715>convex

Perple_X release 7.1.5, Dec 1, 2023.
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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:

```
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
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
GFSM              F       [F] T GFSM/special_component toggle
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_ion_H+          T       [T] F => use OH-
aq_oxide_components    F       [F] T
aq_solvent_solvus      T       [T] F
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   foTL   mcpv   cmpv   foHL   qHL

Summary of saturated-component entities:
 for: CaO
   lime   cc   arag   limL

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

warning ver079 univeq failed on an edge for the following equilibrium. Probable cause is extreme independent variable limits (e.g., xco2=0) or poor convergence criteria in the thermodynamic data file. In routine:COFACE
finished with equilibrium (1) dol = br
Testing divariant assemblage   2,   2 assemblages remaining to be tested.

warning ver079 univeq failed on an edge for the following equilibrium. Probable cause is extreme independent variable limits (e.g., xco2=0) or poor convergence criteria in the thermodynamic data file. In routine:COFACE
finished with equilibrium (2) tr = atg di
Testing divariant assemblage   3,   3 assemblages remaining to be tested.
finished with equilibrium (3) q = wo
finished with equilibrium (4) di = wo fo
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\Perplex715>psvdraw

Perple_X release 7.1.5, Dec 1, 2023.
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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
```
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
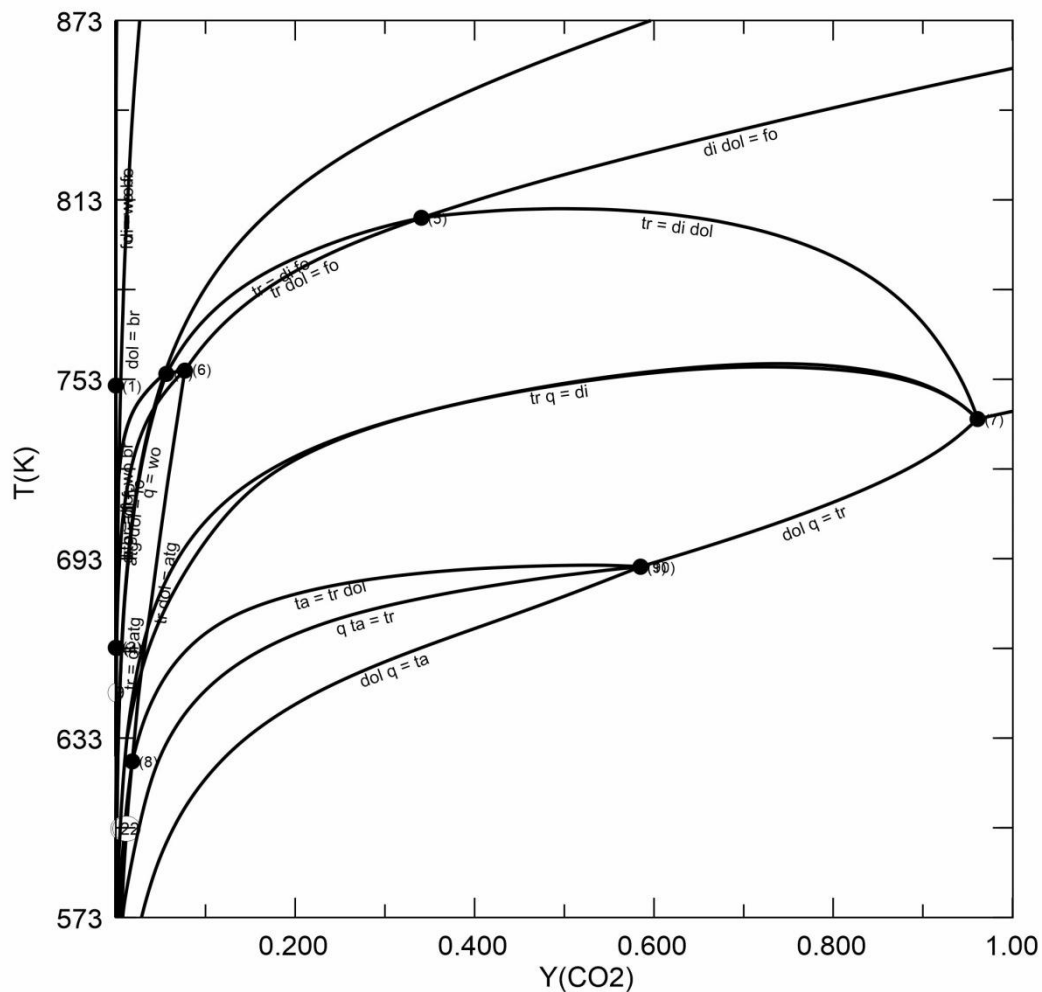
Ex. 5.2 – Isobaric T-XCO₂ pseudosection of a siliceous dolomite for the composition 2Qz–2Dol–1Cal (see Bucher & Grapes, 2011; Fig. 6.8)

(1) Definition of the problem (BUILD)

C:\PERPLEX\Perplex715>build

Perple_X release 7.1.5, Dec 1, 2023.
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NO is the default (blank) answer to all Y/N prompts

Enter a name for this project (the name will be used as the root for all output file names) [default = my_project]:
ex5_2

The problem definition file will be named: ex5_2.dat

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

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

Reading Perple_X options from: perplex_option.dat

The current data base components are:
Na2O MgO Al2O3 SiO2 K2O CaO TiO2 MnO FeO NiO ZrO2 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

Because the thermodynamic data file identifies: H2O CO2 as special components, you will be prompted next for the EoS to be used for the corresponding composants and mixtures thereof. To override this behavior, e.g., to use a generic hybrid fluid EoS (GFSM) either:
   set/add the GFSM option to T in your option file
   or delete the special_component section from the thermodynamic data file header.
NOTE: the EoS choice specified here will override the EoS choice specified by the hybrid_EoS option, tooverride this behavior delete the special_component section from the the thermodynamic data file header.

Select fluid equation of state:
   0 - X(CO2) H2O-CO2 Modified Redlich-Kwong (MRK) DeSantis et al 74
   1 - X(CO2) H2O-CO2 HSMRK Kerrick & Jacobs 81
   2 - X(CO2) H2O-CO2 MRK hybrid-EoS*
   5 - X(CO2) H2O-CO2 CORK Holland & Powell 91, 98
   8 - f(O2/CO2) C-buffered COH MRK hybrid-EoS*
   10 - X(O) C-buffered COH MRK hybrid-EoS Connolly & Cesare 93*
   12 - X(O)-f(S2) C-buffered COHS MRK hybrid-EoS Connolly & Cesare 93*
   13 - X(H2) H2O-H2 MRK hybrid-EoS*
   14 - X(CO2) H2O-CO2 Pitzer & Sterner 94; Holland & Powell mixing 03
   15 - X(H2) H2O-H2 low T MRK hybrid-EoS*
   16 - X(O) H-O MRK hybrid-EoS*
   17 - X(O)-f(S2) H-O-S MRK hybrid-EoS*
   19 - X(O)-X(S) C-buffered COHS MRK hybrid-EoS Connolly & Cesare 93*
   20 - X(O)-X(C) COHS MRK hybrid-EoS Connolly & Cesare 93*
   24 - f(O2/CO2)-N/C C-buffered COHN MRK hybrid-EoS*
   25 - X(CO2)-X(NaCl) H2O-CO2-NaCl Aranovich et al 10
   26 - X(O) O-Si MRK Connolly 16
   27 - X(O)-X(C) C-O-H MRK hybrid-EoS*
*Hybrid EoS use the following pure species EoS, to change these associations modify the hybrid_EoS keywords in the perplex_option file:
      H2O - PSEoS Pitzer & Sterner 1994
      CO2 - PSEoS Pitzer & Sterner 1994
      CH4 - 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	10	10	10 x 10 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: 2SiO2 + 2MgO + 3CaO

Enter the molar amounts of the components:

 MgO CaO SiO2

for the bulk composition of interest:

2

3

2

Output a print file (Y/N)?

y

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

Y

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

N

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

Same as in Ex. 5_1:

rnk | rankinite Ca3Si2O7

lrn | larnite Ca2SiO4

cstn | "Si-titanite" CaSi2O5 (one Si replaces Ti)

```
ty               | tilleyte Ca5Si2O7(CO3)2
spu              | spurrite Ca5Si2O8(CO3)
ak               | akermanite Ca2MgSi2O7
merw             | merwinite Ca3MgSi2O8
mont             | monticellite CaMgSiO4
chum             | clinohumite Mg9Si4O16(OH)2
cen              | clinoenstatite Mg2Si2O6

Include solution models (Y/N)?
n

Enter calculation title:
ex5_2
```

(2) Doing the calculation (VERTEX)

Run VERTEX to make the calculation:

C:\PERPLEX\Perplex715>vertex

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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
refinement_switch   F   [T] F
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   10 / 40 [10/40] >0, <2048; effective x-resolution   10 / 313 nodes
y_nodes   10 / 40 [10/40] >0, <2048; effective y-resolution   10 / 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:
```
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
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
GFSM   F   [F] T GFSM/special_component toggle
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_ion_H+   T   [T] F => use OH-
aq_oxide_components   F   [F] T
aq_solvent_solvus   T   [T] F
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  foTL  mcpv   cmpv   foHL   qHL
----------------------------------------------------------------------------
```

warning ver099 no data for aqueous species, aq_output and aq_lagged_speciation disabled.
** Starting exploratory computational stage **
 2.5% done with low level grid.
 5.0% done with low level grid.
 7.5% done with low level grid.
10.0% done with low level grid.
12.5% done with low level grid.
15.0% done with low level grid.
17.5% done with low level grid.
20.0% done with low level grid.
22.5% done with low level grid.
25.0% done with low level grid.
27.5% done with low level grid.
30.0% done with low level grid.
32.5% done with low level grid.
35.0% done with low level grid.
37.5% done with low level grid.
40.0% done with low level grid.
42.5% done with low level grid.
45.0% done with low level grid.
47.5% done with low level grid.
50.0% done with low level grid.
52.5% done with low level grid.
55.0% done with low level grid.
57.5% done with low level grid.
60.0% done with low level grid.
62.5% done with low level grid.
65.0% done with low level grid.
67.5% done with low level grid.
70.0% done with low level grid.
72.5% done with low level grid.
75.0% done with low level grid.

77.5% done with low level grid.
80.0% done with low level grid.
82.5% done with low level grid.
85.0% done with low level grid.
87.5% done with low level grid.
90.0% done with low level grid.
92.5% done with low level grid.
95.0% done with low level grid.
97.5% done with low level grid.
100.0% done with low level grid.

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 **
 2.5% done with low level grid.
 5.0% done with low level grid.
 7.5% done with low level grid.
10.0% done with low level grid.
12.5% done with low level grid.
15.0% done with low level grid.
17.5% done with low level grid.
20.0% done with low level grid.
22.5% done with low level grid.
25.0% done with low level grid.
27.5% done with low level grid.
30.0% done with low level grid.
32.5% done with low level grid.
35.0% done with low level grid.
37.5% done with low level grid.
40.0% done with low level grid.
42.5% done with low level grid.
45.0% done with low level grid.

47.5% done with low level grid.
50.0% done with low level grid.
52.5% done with low level grid.
55.0% done with low level grid.
57.5% done with low level grid.
60.0% done with low level grid.
62.5% done with low level grid.
65.0% done with low level grid.
67.5% done with low level grid.
70.0% done with low level grid.
72.5% done with low level grid.
75.0% done with low level grid.
77.5% done with low level grid.
80.0% done with low level grid.
82.5% done with low level grid.
85.0% done with low level grid.
87.5% done with low level grid.
90.0% done with low level grid.
92.5% done with low level grid.
95.0% done with low level grid.
97.5% done with low level grid.
100.0% done with low level grid.

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   0.78125E-03   6.5
  Dynamic G calculation   0.0000   0.0
  Static LP   0.78125E-03   6.5
  Dynamic LP   0.0000   0.0
  Successive QP   0.0000   0.0
  Total of above   0.15625E-02   13.0
  Total elapsed time   0.11979E-01   100.0

End of job: ex5_2
----

(3) Plotting the calculated phase diagram (PSSECT)

Run PSSECT to plot the calculated pseudosection:

C:\PERPLEX\Perplex715>pssect

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

Reading Perple_X options from: perplex_option.dat

Perple_X plot options are currently set as:
```
   Keyword:          Value:    Permitted values [default]:
   axis_label_scale     1.20      [1.2] (rel)
   bounding_box :
                    0      [0] x-min (pts)
                    0      [0] y-min (pts)
                  800    [800] x-length (pts)
                  800    [800] y-length (pts)
   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
```
To change these options edit or create the plot option file
See: www.perplex.ethz.ch/perplex_plot_options.html

PostScript will be written to file: ex5_2.ps

Modify the default plot (y/n)?
N

Comparison between projection and pseudosection

Comparison between the isobaric T-X(CO₂) projection for a generic siliceous dolomite containing excess calcite (Ex. 5.1) and the pseudosection calculated for a bulk composition MgO=2, CaO=3, SiO2=2 mol% (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(CO₂) 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
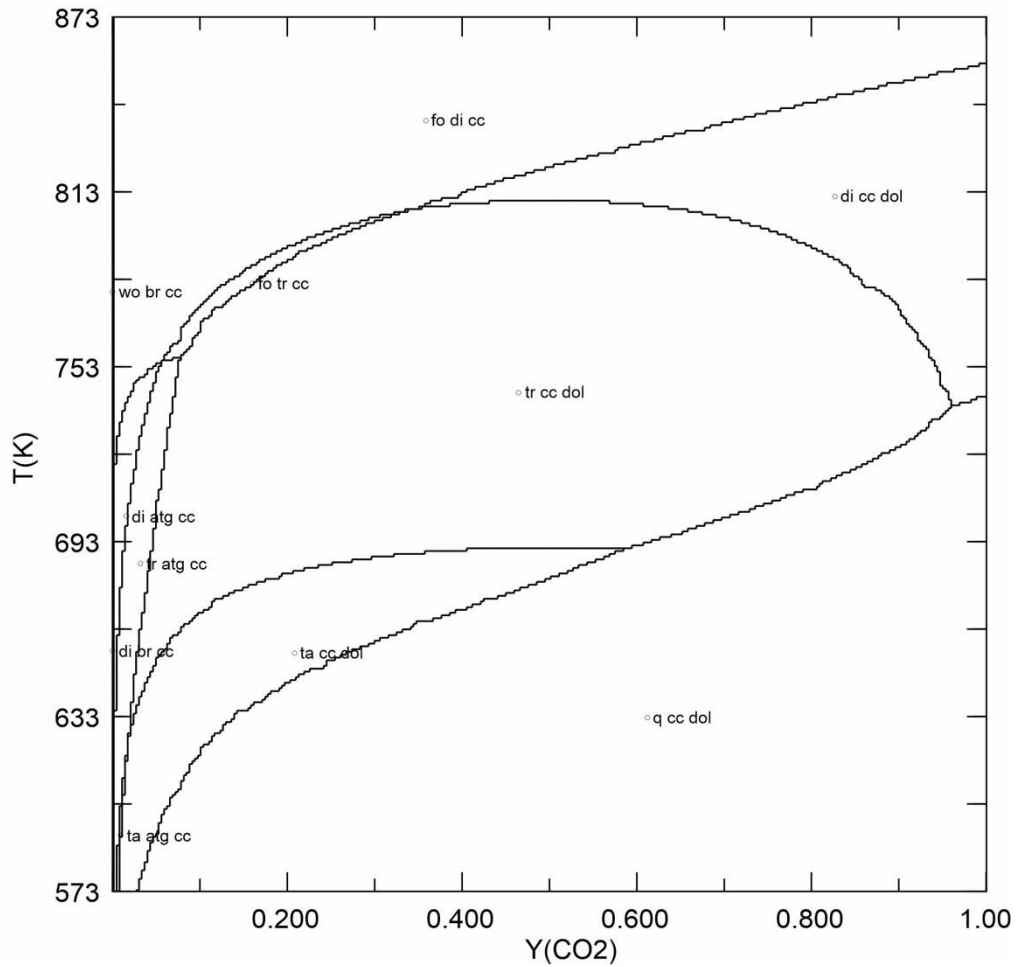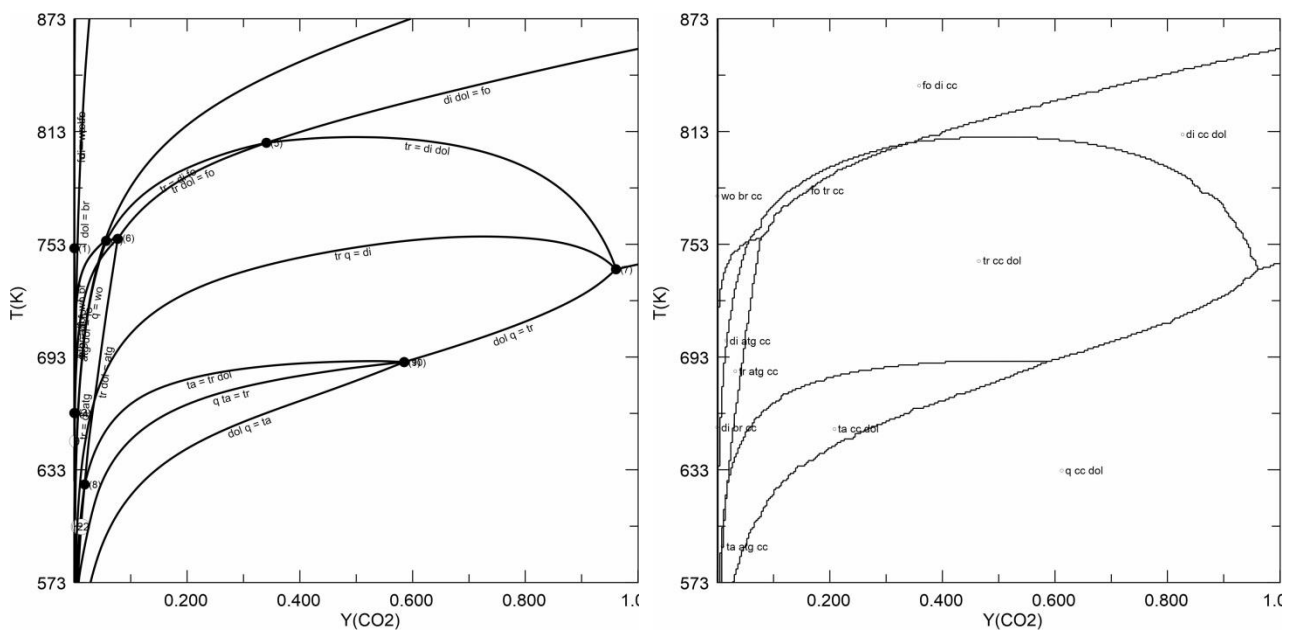
begin saturated component list
SiO2   0  0.00000        0.00000         0.00000      unconstrained amount
end saturated component list
```

(2) Doing the calculation (CONVEX)

Run CONVEX to make the calculation:

C:\PERPLEX\Perplex715>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:
```
 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
 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
 GFSM                  F         [F] T GFSM/special_component toggle
 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_ion_H+             T         [T] F => use OH-
 aq_oxide_components    F         [F] T
 aq_solvent_solvus     T         [T] F
 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   foTL   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\Perplex715>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

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-XCO₂ 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\Perplex715>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
refinement_switch      F       [T] F
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        10 / 40  [10/40] >0, <2048; effective x-resolution   10 / 313 nodes
 y_nodes        10 / 40  [10/40] >0, <2048; effective y-resolution   10 / 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:
 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
 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
 GFSM              F        [F] T GFSM/special_component toggle
 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_ion_H+         T        [T] F => use OH-
 aq_oxide_components   F        [F] T
 aq_solvent_solvus     T        [T] F
 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    foTL    mcpv    cmpv    foHL    qHL
--------------------------------------------------------------------------------
**warning ver099**  no data for aqueous species, aq_output and aq_lagged_speciation disabled.
** Starting exploratory computational stage **
 2.5% done with low level grid.
 5.0% done with low level grid.
 7.5% done with low level grid.
10.0% done with low level grid.
12.5% done with low level grid.
15.0% done with low level grid.
17.5% done with low level grid.
20.0% done with low level grid.
22.5% done with low level grid.
25.0% done with low level grid.
27.5% done with low level grid.
30.0% done with low level grid.
32.5% done with low level grid.
35.0% done with low level grid.
37.5% done with low level grid.
40.0% done with low level grid.
42.5% done with low level grid.
45.0% done with low level grid.
47.5% done with low level grid.
50.0% done with low level grid.
52.5% done with low level grid.
55.0% done with low level grid.
57.5% done with low level grid.
60.0% done with low level grid.
62.5% done with low level grid.
65.0% done with low level grid.
67.5% done with low level grid.
70.0% done with low level grid.
```

72.5% done with low level grid.
75.0% done with low level grid.
77.5% done with low level grid.
80.0% done with low level grid.
82.5% done with low level grid.
85.0% done with low level grid.
87.5% done with low level grid.
90.0% done with low level grid.
92.5% done with low level grid.
95.0% done with low level grid.
97.5% done with low level grid.
100.0% done with low level grid.

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 **
  2.5% done with low level grid.
  5.0% done with low level grid.
  7.5% done with low level grid.
 10.0% done with low level grid.
 12.5% done with low level grid.
 15.0% done with low level grid.
 17.5% done with low level grid.
 20.0% done with low level grid.
 22.5% done with low level grid.
 25.0% done with low level grid.
 27.5% done with low level grid.
 30.0% done with low level grid.
 32.5% done with low level grid.
 35.0% done with low level grid.
 37.5% done with low level grid.
 40.0% done with low level grid.
 42.5% done with low level grid.
 45.0% done with low level grid.

47.5% done with low level grid.
50.0% done with low level grid.
52.5% done with low level grid.
55.0% done with low level grid.
57.5% done with low level grid.
60.0% done with low level grid.
62.5% done with low level grid.
65.0% done with low level grid.
67.5% done with low level grid.
70.0% done with low level grid.
72.5% done with low level grid.
75.0% done with low level grid.
77.5% done with low level grid.
80.0% done with low level grid.
82.5% done with low level grid.
85.0% done with low level grid.
87.5% done with low level grid.
90.0% done with low level grid.
92.5% done with low level grid.
95.0% done with low level grid.
97.5% done with low level grid.
100.0% done with low level grid.

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   0.10417E-02   9.8
  Dynamic G calculation   0.0000   0.0
  Static LP   0.26042E-03   2.4
  Dynamic LP   0.0000   0.0
  Successive QP   0.0000   0.0
  Total of above   0.13021E-02   12.2
  Total elapsed time   0.10677E-01   100.0

End of job: ex5_4
----

(3) Plotting the calculated phase diagram (PSSECT)

Run PSSECT to plot the calculated pseudosection:

C:\PERPLEX\Perplex715>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
```
To change these options edit or create the plot option file
See: www.perplex.ethz.ch/perplex_plot_options.html

PostScript will be written to file: ex5_4.ps
Modify the default plot (y/n)?
N

Comparison between projections and pseudosections

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

Ex 6

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

This exercise explains how to calculate *solvus* relations in the system CaCO₃-MgCO₃. 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 MgCO₃ in calcite in equilibrium with dolomite, and that of CaCO₃ 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 CaCO₃–MgCO₃ system, at CO₂ 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, <u>SOLID SOLUTIONS MUST NOW BE CONSIDERED</u>. Perplex deals with solid solutions by creating a whole set of "pseudocompounds" (intermediate compositions), and treating each of them like a separate phase.** Thus, if a carbonate with composition Cal₉₀ has a lower free energy than Cal₉₅ at a particular P-T condition, Cal₉₀ 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\Perplex715>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]:
ex6_5kbar

The problem definition file will be named: ex6_5kbar.dat

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

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

Because the thermodynamic data file identifies: CO2 as special components, you will be prompted next for the EoS to be used for the corresponding composants and mixtures thereof. To override this behavior, e.g., to use a generic hybrid fluid EoS (GFSM) either:
  set/add the GFSM option to T in your option file
  or delete the special_component section from the thermodynamic data file header.
NOTE: the EoS choice specified here will override the EoS choice specified by the hybrid_EoS option, tooverride this behavior delete the special_component section from the the thermodynamic data file header.

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

Do(AE)

Cc(AE)

Do(AE) and Cc(AE) are the solution models for dolomite and magnesite from Anovitz & Essene (1987), respectively. Cc(AE) also models Mg-calcite.

"The Do(AE) model requires <u>fictive do-structure endmembers</u> 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\Perplex715>vertex

Perple_X release 7.1.5, Dec 1, 2023.
Copyright (C) 1986-2023 James A D Connolly <www.perplex.ethz.ch/copyright.html>.

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

Reading problem definition from file: ex6_5kbar.dat
Reading thermodynamic data from file: hp62ver.dat
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
   refinement_switch   F   [T] F
   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          10 / 40   [10/40] >0, <2048; effective x-resolution   10 / 313 nodes
y_nodes          10 / 40   [10/40] >0, <2048; effective y-resolution   10 / 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:
```
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
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
GFSM                  F        [F] T GFSM/special_component toggle
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_ion_H+             T        [T] F => use OH-
aq_oxide_components   F        [F] T
aq_solvent_solvus     T        [T] F
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.

warning ver533 CO2 is a molecular fluid species the presence of which is inconsistent with saturated phase component constraints if the saturated phase is a fluid. Possible courses of action are:
    1) exclude CO2   and restart.
    2) remove the phase saturation constraint and restart.
    3) ignore this warning and continue execution.

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

We are considering a simplified system, assuming that fluid is pure CO2 and that CO2 is a saturated fluid phase.

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 **
  9.1% done with low level grid.

18.2% done with low level grid.
27.3% done with low level grid.
36.4% done with low level grid.
45.5% done with low level grid.
54.5% done with low level grid.
63.6% done with low level grid.
72.7% done with low level grid.
81.8% done with low level grid.
90.9% done with low level grid.

Exploratory stage generated:
    14 compositions for: Do(AE)
    22 compositions for: Cc(AE)
Total number of compositions: 36

This is the beginning of the AUTO-REFINE STAGE
** Starting auto_refine computational stage **
 2.5% done with low level grid.
 5.0% done with low level grid.
 7.5% done with low level grid.
10.0% done with low level grid.
12.5% done with low level grid.
15.0% done with low level grid.
17.5% done with low level grid.
20.0% done with low level grid.
22.5% done with low level grid.
25.0% done with low level grid.
27.5% done with low level grid.
30.0% done with low level grid.
32.5% done with low level grid.
35.0% done with low level grid.
37.5% done with low level grid.
40.0% done with low level grid.
42.5% done with low level grid.
45.0% done with low level grid.
47.5% done with low level grid.
50.0% done with low level grid.
52.5% done with low level grid.
55.0% done with low level grid.
57.5% done with low level grid.
60.0% done with low level grid.
62.5% done with low level grid.
65.0% done with low level grid.
67.5% done with low level grid.
70.0% done with low level grid.
72.5% done with low level grid.
75.0% done with low level grid.
77.5% done with low level grid.
80.0% done with low level grid.

82.5% done with low level grid.
85.0% done with low level grid.
87.5% done with low level grid.
90.0% done with low level grid.
92.5% done with low level grid.
95.0% done with low level grid.
97.5% done with low level grid.
100.0% done with low level grid.

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   0.39062E-02   17.6
  Static LP   0.26042E-03   1.2
  Dynamic LP   0.10417E-02   4.7
  Successive QP   0.52083E-02   23.5
  Total of above   0.10417E-01   47.1
  Total elapsed time   0.22135E-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\Perplex715>pssect

Perple_X release 7.1.5, Dec 1, 2023.
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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

warning ver533 CO2   is a molecular fluid species the presence of which is inconsistent with saturated phase component constraints if the saturated phase is a fluid. Possible courses of action are:
   1) exclude CO2   and restart.
   2) remove the phase saturation constraint and restart.
   3) ignore this warning and continue execution.

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

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

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

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

5kbar

> 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 10 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\Perplex715>build

Perple_X release 7.1.5, Dec 1, 2023.
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NO is the default (blank) answer to all Y/N prompts

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

The problem definition file will be named: ex7.dat

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

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

Because the thermodynamic data file identifies: CO2 as special components, you will be prompted next for the EoS to be used for the corresponding composants and mixtures thereof. To override this behavior, e.g., to use a generic hybrid fluid EoS (GFSM) either:
  set/add the GFSM option to T in your option file
  or delete the special_component section from the thermodynamic data file header.
NOTE: the EoS choice specified here will override the EoS choice specified by the hybrid_EoS option, tooverride this behavior delete the special_component section from the the thermodynamic data file header.

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

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

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

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

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

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

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

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

  H2O - PSEoS Pitzer & Sterner 1994

  CO2 - PSEoS Pitzer & Sterner 1994

  CH4 - 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 see: www.perplex.ethz.ch/perplex_solution_model_glossary.html

or read the commentary in the solution model file.

Do(AE)

Cc(AE)

Same as in Ex. 6

Enter calculation title:

ex7

(2) Doing the calculation (CONVEX)

Run CONVEX to make the calculation:

C:\PERPLEX\Perplex715>convex

Perple_X version 6.9.1, source updated January 3, 2022.

Copyright (C) 1986-2022 James A D Connolly <www.perplex.ethz.ch/copyright.html>.

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

ex7

Reading problem definition from file: ex7.dat

Reading thermodynamic data from file: 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:

  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

  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

  GFSM   F   [F] T GFSM/special_component toggle

  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_ion_H+   T   [T] F => use OH-

  aq_oxide_components   F   [F] T

  aq_solvent_solvus   T   [T] F

  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
```

warning ver533 CO2   is a molecular fluid species the presence of which is inconsistent with saturated phase component constraints if the saturated phase is a fluid. Possible courses of action are:

   1) exclude CO2   and restart.
   2) remove the phase saturation constraint and restart.
   3) ignore this warning and continue execution.

Continue execution despite this warning (Y/N)?

y

```
-------------------------------------------------------------------------------
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

warning ver533 CO2   is a molecular fluid species the presence of which is inconsistent with saturated phase component constraints if the saturated phase is a fluid. Possible courses of action are:

   1) exclude CO2   and restart.

   2) remove the phase saturation constraint and restart.

   3) ignore this warning and continue execution.

Continue execution despite this warning (Y/N)?

y

To automatically answer interactive warnings affirmatively, set warn_interactive to false.

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\Perplex715>psvdraw

Perple_X release 7.1.5, Dec 1, 2023.
Copyright (C) 1986-2023 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
```
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.

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)

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)

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

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

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

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

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

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

Ex 8

Ex. 8 – 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 H2O, SiO2 (q), KAl3O5 (mu) into the sub-composition MgO-FeO-Al2O3.

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

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

---

(1) Definition of the problem (BUILD)

C:\PERPLEX\Perplex715>build

Perple_X release 7.1.5, Dec 1, 2023.
Copyright (C) 1986-2023 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 = hp02ver.dat]:
hp62ver.dat

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

Reading Perple_X options from: perplex_option.dat

The current data base components are:

Na2O MgO Al2O3 SiO2 K2O CaO TiO2 MnO FeO   NiO ZrO2 Cl2 O2 H2O CO2 CuO Cr2O3 S2 F2 N2 ZnO
Transform them (Y/N)?

y

Three new components should be defined here:

MU = 0.5 K2O + 1.5 Al2O3

PHL = 3 MgO - Al2O3

ANN (=3 FeO - Al2O3)

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

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

MU

Enter old component to be replaced with MU   :

K2O

Enter other components (< 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: KAl3Si3O10(OH)2; if SiO2 and H2O are considered in excess, its composition is defined by 0.5 K2O + 1.5 Al2O3 (KAl3O5)

0.5

1.5

 MU   = 0.50 K2O   1.50 Al2O3
Is this correct (Y/N)?

y

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

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

Y

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

PHL

Enter old component to be replaced with PHL :

MgO

Enter other components (< 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: KMg3AlSi3O10(OH)2. Considering H2O, SiO2 and KAl3O5 in excess, its composition is defined as PHL = (3MgO − Al2O3) or, reduced, PHL = (1.5MgO − 0.5Al2O3).

1.5

-0.5

 PHL =   1.50 MgO   -0.50 Al2O3

Is this correct (Y/N)?

y

The current data base components are:

Na2O PHL Al2O3 SiO2 MU CaO TiO2 MnO   FeO   NiO ZrO2 Cl2 O2 H2O CO2 CuO Cr2O3 S2 F2 N2 ZnO

Transform them (Y/N)?

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

Y

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

ANN

Enter old component to be replaced with ANN :

FeO

Enter other components (< 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
SiO2 and MU (KAl3O5) 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.

Because the thermodynamic data file identifies: H2O as special components, you will be prompted next for the EoS to be used for the corresponding composants and mixtures thereof. To override this behavior, e.g., to use a generic hybrid fluid EoS (GFSM) either:
  set/add the GFSM option to T in your option file
  or delete the special_component section from the thermodynamic data file header.
NOTE: the EoS choice specified here will override the EoS choice specified by the hybrid_EoS option, tooverride this behavior delete the special_component section from the the thermodynamic data file header.

Select fluid equation of state:
  0 - X(CO2) H2O-CO2 Modified Redlich-Kwong (MRK) DeSantis et al 74
  1 - X(CO2) H2O-CO2 HSMRK Kerrick & Jacobs 81

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

    H2O - PSEoS Pitzer & Sterner 1994

    CO2 - PSEoS Pitzer & Sterner 1994

    CH4 - 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 see: www.perplex.ethz.ch/perplex_solution_model_glossary.html or read the commentary
in the solution model file.
Chl(W)
Bi(W)
Gt(W)
Ctd(W)
St(W)
Crd(W)

Enter calculation title:
Ex8

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

Specify values for:
      P(bar)   T(K)   Y(CO2)
For calculation 1, enter zeros to finish.
8000
843
0

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

Specify values for:
      P(bar)   T(K)   Y(CO2)

For calculation 3, enter zeros to finish.
8000
863
0

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

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

(2) Doing the calculation (CONVEX)

Run CONVEX to make the calculation:

C:\PERPLEX\Perplex715>convex

Perple_X release 7.1.5, Dec 1, 2023.
Copyright (C) 1986-2023 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
 refinement_switch      F      [T] F
 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:
 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
 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
 GFSM                   F      [F] T GFSM/special_component toggle
 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_ion_H+              T      [T] F => use OH-
 aq_oxide_components    F      [F] T
 aq_solvent_solvus      T      [T] F
 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   foTL   faTL    cfsg    mfpv    cmpv    cfpv    capv    fcor    hmgts   foHL    faHL   qHL
```


Summary of saturated-component entities:

for: SiO2

```
 q     trd    crst   coe    stv    qL    q8L    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 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)?
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\Perplex715>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
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

P(bar) =0.800E+04
T(K) = 843.
Y(CO2) = 0.00
(fluid saturated)

ky

fsst1248 + q mu

alm_alm_Chl_Crd_028

ann   phl

P(bar) =0.800E+04
T(K) = 853.
Y(CO2) = 0.00
(fluid saturated)

ky

fsst1859 + q mu

alm_alm_Chl_Crd_026

ann   phl

P(bar) =0.800E+04
T(K) = 863.
Y(CO2) = 0.00
(fluid saturated)

ky

fsst2490 + q mu

alm_alm_88.0_Chl_Crd_3924

ann   phl

P(bar) =0.800E+04
T(K) = 873.
Y(CO2) = 0.00
(fluid saturated)

ky

fsst3824 + q mu

alm_alm_87.4_Crd_230092

ann   phl

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).

Ky
St
Grt   Chl
Bt

P = 8 kbar
T = 570°C
+Qz +Mu +H$_2$O

Ky
St
Grt   Chl
Bt

P = 8 kbar
T = 580°C
+Qz +Mu +H$_2$O

Ky
St
Grt   Chl
Bt

P = 8 kbar
T = 590°C
+Qz +Mu +H$_2$O

Ky
St
Grt   Chl
Bt

P = 8 kbar
T = 600°C
+Qz +Mu +H$_2$O

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\Perplex715>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 = hp02ver.dat]:
hp62ver.dat

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

Reading Perple_X options from: perplex_option.dat

The current data base components are:
Na2O MgO Al2O3 SiO2 K2O CaO TiO2 MnO FeO NiO ZrO2 Cl2 O2 H2O CO2 CuO Cr2O3 S2 F2 N2 ZnO

Transform them (Y/N)?

n

Specify computational mode:
    1 - Convex-Hull minimization
    2 - Constrained minimization on a 2d grid [default]
    3 - Constrained minimization on a 1d grid
    4 - Output pseudocompound data
    5 - 1-d Phase fractionation
    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

Because the thermodynamic data file identifies: H2O as special components, you will be prompted next for the EoS to be used for the corresponding composants and mixtures thereof. To override this behavior, e.g., to use a generic hybrid fluid EoS (GFSM) either:
  set/add the GFSM option to T in your option file
  or delete the special_component section from the thermodynamic data file header.
NOTE: the EoS choice specified here will override the EoS choice specified by the hybrid_EoS option, tooverride this behavior delete the special_component section from the the thermodynamic data file header.

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

Chl(W)

Bi(W)

Gt(W)

Ctd(W)

St(W)

Crd(W)

Enter calculation title:

Ex9

(2) Doing the calculation (VERTEX)

Run VERTEX to make the calculation:

C:\PERPLEX\Perplex715>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
 refinement_switch     F       [T] F
 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          10 / 60   [10/40] >0, <2048; effective x-resolution  10 / 473 nodes
 y_nodes          10 / 60   [10/40] >0, <2048; effective y-resolution  10 / 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:
 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
 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
 GFSM            F       [F] T GFSM/special_component toggle
 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_ion_H+         T       [T] F => use OH-
 aq_oxide_components    F       [F] T
 aq_solvent_solvus     T       [T] F
 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   foTL   faTL   cfsg   mfpv   cmpv   cfpv   capv   fcor   hmgts   kjdh   foHL   faHL
 qHL   kjL
-------------------------------------------------------------------------------
-------------------------------------------------------------------------------
Summary of saturated-component entities:
 for: SiO2
   q    trd    crst    coe    stv    qL    q8L    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 **
  9.1% done with low level grid.
 18.2% done with low level grid.
 27.3% done with low level grid.
 36.4% done with low level grid.
 45.5% done with low level grid.
 54.5% done with low level grid.
 63.6% done with low level grid.
 72.7% done with low level grid.
 81.8% done with low level grid.
 90.9% done with low level grid.

Exploratory stage generated:
     33 compositions for: Chl(W)
      7 compositions for: Gt(W)
      5 compositions for: Ctd(W)
      8 compositions for: St(W)
     62 compositions for: Bi(W)
     27 compositions for: Crd(W)
Total number of compositions: 142

** Starting auto-refine computational stage **
  1.7% done with low level grid.
  3.3% done with low level grid.
  5.0% done with low level grid.
  6.7% done with low level grid.
  8.3% done with low level grid.
 10.0% done with low level grid.
 11.7% done with low level grid.
 13.3% done with low level grid.
 15.0% done with low level grid.
 16.7% done with low level grid.
 18.3% done with low level grid.

20.0% done with low level grid.
21.7% done with low level grid.
23.3% done with low level grid.
25.0% done with low level grid.
26.7% done with low level grid.
28.3% done with low level grid.
30.0% done with low level grid.
31.7% done with low level grid.
33.3% done with low level grid.
35.0% done with low level grid.
36.7% done with low level grid.
38.3% done with low level grid.
40.0% done with low level grid.
41.7% done with low level grid.
43.3% done with low level grid.
45.0% done with low level grid.
46.7% done with low level grid.
48.3% done with low level grid.
50.0% done with low level grid.
51.7% done with low level grid.
53.3% done with low level grid.
55.0% done with low level grid.
56.7% done with low level grid.
58.3% done with low level grid.
60.0% done with low level grid.
61.7% done with low level grid.
63.3% done with low level grid.
65.0% done with low level grid.
66.7% done with low level grid.
68.3% done with low level grid.
70.0% done with low level grid.
71.7% done with low level grid.
73.3% done with low level grid.
75.0% done with low level grid.
76.7% done with low level grid.
78.3% done with low level grid.
80.0% done with low level grid.
81.7% done with low level grid.
83.3% done with low level grid.
85.0% done with low level grid.
86.7% done with low level grid.
88.3% done with low level grid.
90.0% done with low level grid.
91.7% done with low level grid.
93.3% done with low level grid.
95.0% done with low level grid.
96.7% done with low level grid.
98.3% done with low level grid.
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
   1043 grid cells to be refined at grid level 3
       ...working (   250 minimizations done)
       ...working (   751 minimizations done)
       ...working (  1252 minimizations done)
       ...working (  1755 minimizations done)
       refinement at level 3 involved   1907 minimizations
   6760 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 (  1353 minimizations done)
       ...working (  1854 minimizations done)
       ...working (  2356 minimizations done)
       ...working (  2857 minimizations done)
       refinement at level 4 involved   2966 minimizations
   9726 minimizations required of the theoretical limit of  224676
-------------------------------------------------------------------------

    Timing              min.      % of total
   Static G calculation     0.67187E-01       8.1
   Dynamic G calculation     0.16953          20.4
   Static LP             0.49479E-02       0.6
   Dynamic LP            0.94531E-01      11.4
   Successive QP          0.45339         54.6
   Total of above         0.78958         95.1
   Total elapsed time     0.83021        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\Perplex715>pssect

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

PostScript will be written to file: ex9.ps

Modify the default plot (y/n)?
n
There are 5 fields for: Bi(W) Crd(W) mu san

Quartz and H₂O 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\Perplex715>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   [F] T
  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
  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    0.1E+05  [1d4] >0; fraction = 0.1E-02  [1d-2]
 Seismic wavespeed computational options:
   seismic_data_file      T      [F] T
   bounds                 VRH    [VRH] HS
   vrh/hs_weighting       0.5    [0.5] 0->1
   explicit_bulk_modulus  T      [T] F
   poisson_ratio          on     [on] all off; Poisson ratio = 0.35
   seismic_output         som    [some] none all
   poisson_test           F      [F] T
   Tisza_test             F      [F] T
   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

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_nodes to obtain the desired resolution.
To disable [all] interactive warnings set warn_interactive to F.

Continue (y/n)?
y
…
…

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   0.586736E-001 0.814659   0.102551E-001 0.171665   0.170888E-002 7.44356   0.314714
5.63422   0.409001   0.695036   0.480104E-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
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\Perplex715>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   [F] T
    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
    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   0.1E+05 [1d4] >0; fraction = 0.1E-02 [1d-2]
  Seismic wavespeed computational options:
    seismic_data_file   T   [F] T
    bounds   VRH   [VRH] HS
    vrh/hs_weighting   0.5   [0.5] 0->1
    explicit_bulk_modulus T   [T] F
    poisson_ratio   on   [on] all off; Poisson ratio = 0.35
    seismic_output   som   [some] none all
    poisson_test   F   [F] T
    Tisza_test   F   [F] T
    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 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_nodes to obtain the desired resolution.
To disable [all] interactive warnings set warn_interactive to F.

Continue (y/n)?
 y
…
…

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 0.117823   0.471855   0.144985   0.313366
max 0.267658   0.638718   0.339166   0.584945
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.

Chl XMg

Bt XMg

Grt XMg

St XMg

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 (Na₂O, 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\Perplex715>vertex

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

ex10

…

(3) Plotting the calculated phase diagram (PSSECT)

Run PSSECT to plot the calculated pseudosection:

C:\PERPLEX\Perplex715>pssect

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

Reading Perple_X options from: perplex_option.dat

Perple_X plot options are currently set as:

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

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   3 fields for: Bi(W) Mica(W) Crd(W) feldspar feldspar
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	2.56869	1.22107	0.00000	0.00000	0.05789	2.15235	2.77893	4.00000
Bi(W)	22.53	20.80	18.34	7.25	0.00000	1.12172	0.64860	0.50000	0.00000	0.02352	1.70616	2.85140	1.00000
Mica(W)	32.05	32.30	31.02	12.3	0.06244	0.03160	1.44626	0.43620	0.00273	0.00000	0.02351	3.05237	1.00000
feldspar	**27.64**	**29.69**	**39.72**	**15.7**	**0.34063**	**0.00000**	**0.65666**	**0.00271**	**0.31332**	**0.00000**	**0.00000**	**2.68668**	**0.00000**

Phase speciation (molar proportions):

Chl(W)   mnchl: 0.01158, daph: 0.46919, ames: 0.22112, afchl: 0.19369, clin: 0.29808, och1: 0.00002, och2: -0.19366
Bi(W)   mnbi: 0.00784, east: 0.14860, ann: 0.55017, phl: 0.23774, obi: 0.05564
Mica(W)   mu: 0.81728, pa: 0.12487, ma1_dqf: 0.00273, cel: 0.03160, fcel: 0.02351
feldspar   abh: 0.68125, an: 0.31332, san: 0.00542

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

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 Perplex715 folder.

Run WERAMI to calculate the MODES of ALL the phases.

C:\PERPLEX\Perplex715>werami

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

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

Perple_X computational option settings for WERAMI:
  Keyword: Value: Permitted values [default]:

Input/Output options:
```
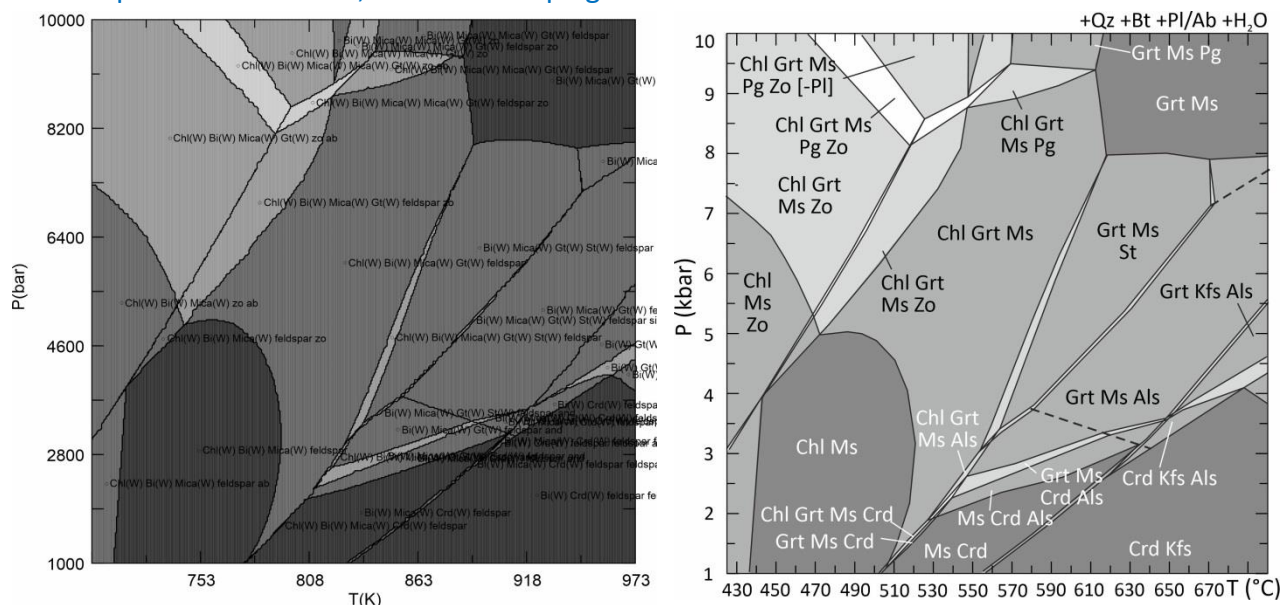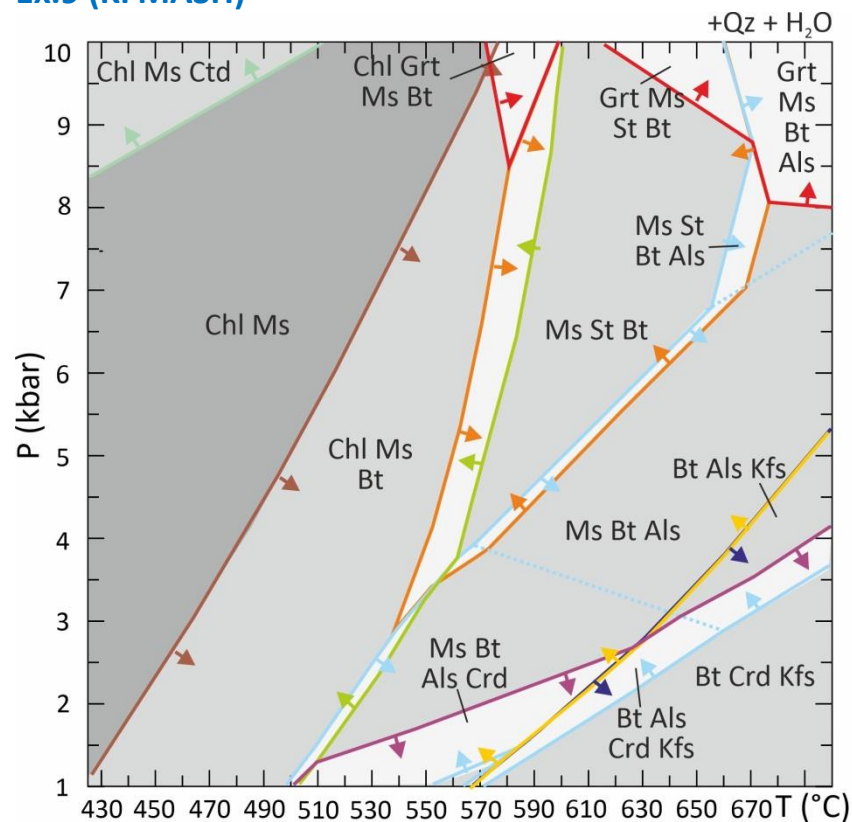 aqueous_output        T      [F] T
 aqeuous_species       20     [20] 0-150
 aq_solvent_composition y      [y] m: y => mol fraction, m => molality
 aq_solute_composition  m      y [m]: y => mol fraction, m => molality
 spreadsheet           T      [F] T
 logarithmic_p         F      [F] T
 logarithmic_X         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
 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   0.1E+05 [1d4] >0; fraction = 0.1E-02  [1d-2]
```
Seismic wavespeed computational options:
```
 seismic_data_file     T      [F] T
 bounds                VRH    [VRH] HS
 vrh/hs_weighting      0.5    [0.5] 0->1
 explicit_bulk_modulus T      [T] F
 poisson_ratio         on     [on] all off; Poisson ratio = 0.35
 seismic_output        som    [some] none all
 poisson_test          F      [F] T
 Tisza_test            F      [F] T
 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   2.58877   13.2457   21.2738   0.100000E+100 27.9160   0.100000E+100 20.1753   0.932452E-001
0.137610E-001 0.100000E+100 0.100000E+100 0.949769   0.100000E+100 0.292668E-002
max   21.5553   37.0092   38.3933   -0.100000E+100 31.3362   -0.100000E+100 20.5351   6.29072
14.8790   -0.100000E+100 -0.100000E+100 5.72414   -0.100000E+100 0.767599

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\Perplex715>build

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

Enter a name for this project (the name will be used as the root for all output file names) [default = my_project]:
ex11

The problem definition file will be named: ex11.dat

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

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

Reading 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

Because the thermodynamic data file identifies: H2O as special components, you will be prompted next for the EoS to be used for the corresponding composants and mixtures thereof. To override this behavior, e.g., to use a generic hybrid fluid EoS (GFSM) either:
  set/add the GFSM option to T in your option file
  or delete the special_component section from the thermodynamic data file header.
NOTE: the EoS choice specified here will override the EoS choice specified by the hybrid_EoS option, tooverride this behavior delete the special_component section from the the thermodynamic data file header.

Select fluid equation of state:
   0 - X(CO2) H2O-CO2 Modified Redlich-Kwong (MRK) DeSantis et al 74
   1 - X(CO2) H2O-CO2 HSMRK Kerrick & Jacobs 81
   2 - X(CO2) H2O-CO2 MRK hybrid-EoS*
   5 - X(CO2) H2O-CO2 CORK Holland & Powell 91, 98
   8 - f(O2/CO2) C-buffered COH MRK hybrid-EoS*
  10 - X(O) C-buffered COH MRK hybrid-EoS Connolly & Cesare 93*
  12 - X(O)-f(S2) C-buffered COHS MRK hybrid-EoS Connolly & Cesare 93*
  13 - X(H2) H2O-H2 MRK hybrid-EoS*
  14 - X(CO2) H2O-CO2 Pitzer & Sterner 94; Holland & Powell mixing 03
  15 - X(H2) H2O-H2 low T MRK hybrid-EoS*
  16 - X(O) H-O MRK hybrid-EoS*
  17 - X(O)-f(S2) H-O-S MRK hybrid-EoS*
  19 - X(O)-X(S) C-buffered COHS MRK hybrid-EoS Connolly & Cesare 93*
  20 - X(O)-X(C) COHS MRK hybrid-EoS Connolly & Cesare 93*
  24 - f(O2/CO2)-N/C C-buffered COHN MRK hybrid-EoS*
  25 - X(CO2)-X(NaCl) H2O-CO2-NaCl Aranovich et al 10
  26 - X(O) O-Si MRK Connolly 16
  27 - X(O)-X(C) C-O-H MRK hybrid-EoS*
*Hybrid EoS use the following pure species EoS, to change these associations modify the hybrid_EoS keywords in the perplex_option file:
    H2O - PSEoS Pitzer & Sterner 1994
    CO2 - PSEoS Pitzer & Sterner 1994
    CH4 - 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   10   10   10 x 10 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\Perplex715>vertex

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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\Perplex715>pssect

Perple_X release 7.1.5, Dec 1, 2023.
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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)

```
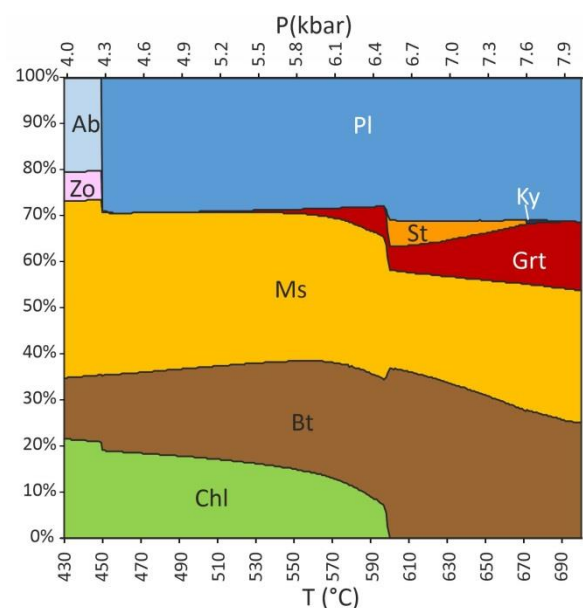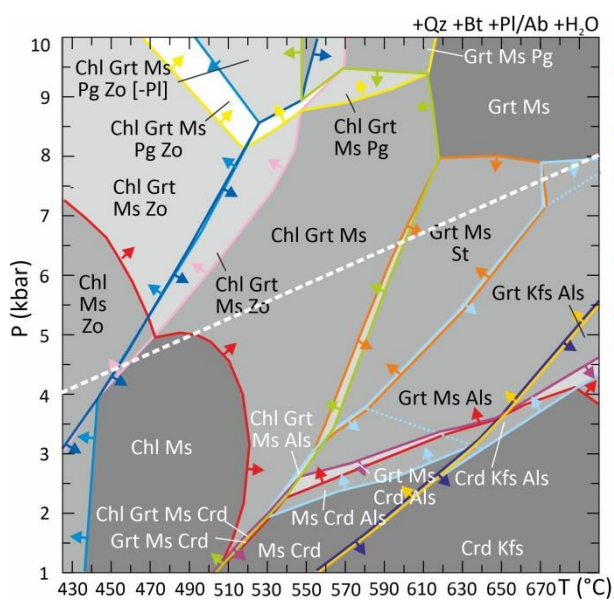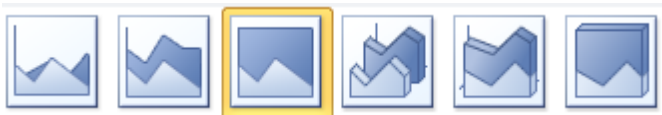font              Helvetica
grid          F       [F] T
half_ticks        T       [T] F
line_width        1.00      0-99 [1.] (pts)
picture_transformation :
                0.180    [0.18] x-scale (rel)
                0.180    [0.18] y-scale (rel)
                130.    [0.18] x-translation (pts)
                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
```
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 17 fields for: Chl Bio Mica Fsp zo ab
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 – DIRECT modelling of an anatectic METAPELITE (NKCFMASH system)

This exercise deals with the "DIRECT" modelling of a metapelite sample at supra-*solidus* conditions (i.e. melt-bearing). "Direct modelling" means that you know which is the protolith composition, <u>including its initial H₂O amount (which is generally not the case...).</u> In other worlds, we will consider a generic metapelite (with an average composition) and we will see what happens to this metapelite if it is heated enough to experience partial melting.

This exercise is based on the paper by White et al. (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\Perplex715>build

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

Enter a name for this project (the name will be used as the root for all output file names) [default = my_project]:
ex12

The problem definition file will be named: ex12.dat

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

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

Reading Perple_X options from: perplex_option.dat

The current data base components are:
Na2O MgO Al2O3 SiO2 K2O CaO TiO2 MnO   FeO   NiO   ZrO2 Cl2 O2 H2O CO2 CuO Cr2O3 S2 F2 N2 ZnO
Transform them (Y/N)?
n

Specify computational mode:
    1 - Convex-Hull minimization

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

3 - Constrained minimization on a 1d grid

4 - Output pseudocompound data

5 - 1-d Phase fractionation

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

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

  set/add the GFSM option to T in your option file

  or delete the special_component section from the thermodynamic data file header.

Select fluid equation of state:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

    H2O - PSEoS Pitzer & Sterner 1994

    CO2 - PSEoS Pitzer & Sterner 1994

    CH4 - 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 - 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	10	10	10 x 10 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
warning ver056 the EoS specified for H2O   by the hybrid_EoS option will be overridden by the EoS specified in the problem definition file. To prevent this behavior set the GFSM option to True.

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 see:www.perplex.ethz.ch/perplex_solution_model_glossary.html or read the commentary in the solution model file.
Bi(W)
Mica(W)
Gt(W)
St(W)
Crd(W)
Opx(W)
feldspar
melt(W)

Enter calculation title:
Ex12

(2) Doing the calculation (VERTEX)

Run VERTEX to make the calculation:

C:\PERPLEX\Perplex715>vertex

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

…

(3) Plotting the calculated phase diagram (PSSECT)

Run PSSECT to plot the calculated pseudosection:

C:\PERPLEX\Perplex715>pssect

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

Reading Perple_X options from: perplex_option.dat

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

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

PostScript will be written to file: ex12.ps
Modify the default plot (y/n)?
n

There are   5 fields for: Bio Mica Fsp Fsp sill q H2O
There are   9 fields for: Bio Crd Opx Fsp Fsp q H2O
There are 10 fields for: Bio Mica Gt Fsp Melt q H2O
There are 11 fields for: Crd Opx Fsp Fsp Melt q H2O

+Qz

(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\Perplex691>werami

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

Reading Perple_X options from: perplex_option.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   [F] T
  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
  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   0.1E+05 [1d4] >0; fraction = 0.1E-02 [1d-2]
 Seismic wavespeed computational options:
  seismic_data_file   T   [F] T
  bounds   VRH   [VRH] HS
  vrh/hs_weighting   0.5   [0.5] 0->1
  explicit_bulk_modulus   T   [T] F
  poisson_ratio   on   [on] all off; Poisson ratio = 0.35
  seismic_output   som   [some] none all
  poisson_test   F   [F] T
  Tisza_test   F   [F] T
  fluid_shear_modulus   T   [T] F
  phi_d   0.36   [0.36] 0->1
 Error/warning control options:

```
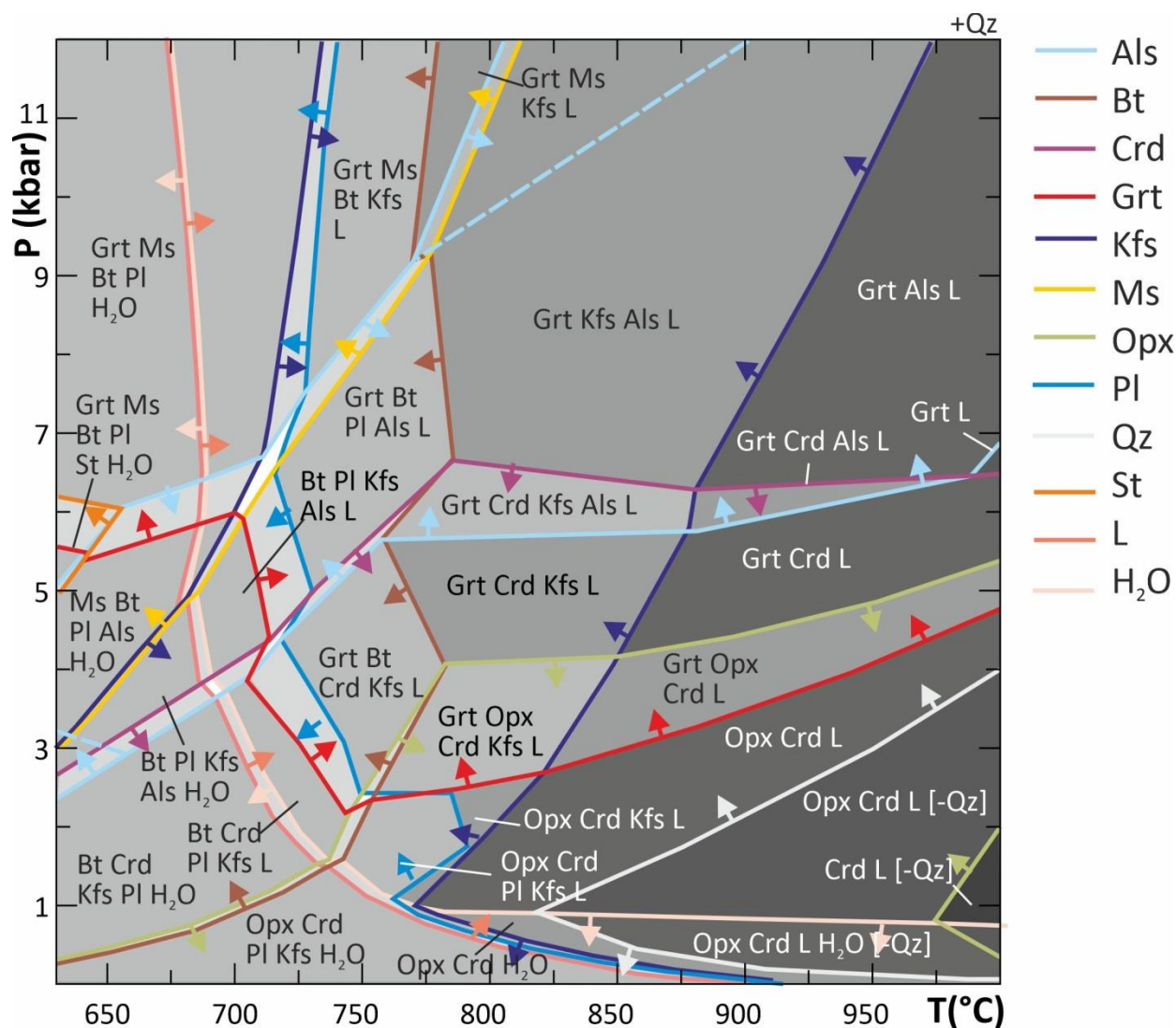pause_on_error        T      [T] F
max_warn_limit        5      [5]
warn_interactive      T      [T] F
aq_error_ver100       F      [F] T, abort during iteration
aq_error_ver101       T      [T] F, solute undersaturation abort
aq_error_ver102       T      [T] F, pure + impure solvent abort
aq_error_ver103       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

warning ver056 the EoS specified for H2O   by the hybrid_EoS option will be overridden by the EoS specified in the problem definition file. To prevent this behavior set the GFSM option to True.

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):

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

…

…

H2O	MgO	Al2O3	SiO2	K2O	CaO	FeO	Na2O
0.000	0.000	0.505	2.990	0.422	0.010	0.000	0.073
0.000	0.000	0.785	2.430	0.009	0.570	0.000	0.206

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

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

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

For example at **973 K (700°C), 8 kbar**:
Stable phases at:
                T(K)   = 973.000
                P(bar) = 8000.00

Phase Compositions (molar proportions):

	wt %	vol %	mol %	mol	H2O	MgO	Al2O3	SiO2	K2O	CaO	FeO	Na2O
Bio	16.90	15.73	4.17	2.26	1.00000	1.19644	0.79434	2.70566	0.50000	0.00000	1.50922	0.00000
Mica	23.41	23.48	6.75	3.65	1.00000	0.05213	1.39949	3.09887	0.45818	0.00329	0.05003	0.04018
Gt	10.84	7.44	2.60	1.40	0.00000	0.53408	1.00000	3.00000	0.00000	0.08760	2.37833	0.00000
Fsp	3.60	3.89	1.56	0.842	0.00000	0.00000	0.58333	2.83335	0.02515	0.16665	0.00000	0.39152
Melt	1.93	2.56	2.15	1.16	0.64995	0.00117	0.13553	1.13085	0.04256	0.00404	0.00381	0.08058
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: 0.29434, ann: 0.52219, phl: 0.24082, obi: -0.05735
 Mica   mu: 0.81420, pa: 0.08035, ma1_dqf: 0.00329, cel: 0.05213, fcel: 0.05003
 Gt   alm: 0.79278, py: 0.17803, gr: 0.02920
 Fsp   abh: 0.78305, an: 0.16665, san: 0.05030
 Melt   fo8L: 0.00029, fa8L: 0.00095, abL: 0.16116, sil8L: 0.00522, anL: 0.00404, kspL: 0.08512, q8L: 0.09327
          h2oL: 0.64995

(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\Perplex715>werami

Perple_X release 7.1.5, Dec 1, 2023.
Copyright (C) 1986-2023 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   [F] T
   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
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    0.1E+05  [1d4] >0; fraction = 0.1E-02  [1d-2]
```
Seismic wavespeed computational options:
```
seismic_data_file      T        [F] T
bounds                 VRH      [VRH] HS
vrh/hs_weighting       0.5      [0.5] 0->1
explicit_bulk_modulus  T        [T] F
poisson_ratio          on       [on] all off; Poisson ratio = 0.35
seismic_output         som      [some] none all
poisson_test           F        [F] T
Tisza_test             F        [F] T
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

warning ver056 the EoS specified for H2O   by the hybrid_EoS option will be overridden by the EoS specified in the problem definition file. To prevent this behavior set the GFSM option to True.

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

...

...

warning ver179 at T(K)= 1203.   P(bar)= 0.1074E+05 the effective expansivity of: q   is negative. Most probably this is because of a Landau ordering model. The Gruneisenthermal parameter and seismic speeds for this phase should be considered with caution.

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	0.141526	2.69477	22.6705	0.284430	0.177312E-001	0.100000E+100				
3.81107	1.17320	0.100000E+100	5.86559	0.100000E+100	2.18090	0.100000E+100	0.100000E+100				
max -0.100000E+100	-0.100000E+100	17.9925	6.97323	48.4425	0.546154	18.3275	-0.100000E+100				
23.9220	4.57976	-0.100000E+100	18.2664	-0.100000E+100	58.4304	-0.100000E+100	-0.100000E+100				

Output has been written to two files:

    plt format is in file: ex12_3.plt

    1d tab format is in file: ex12_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

At the end, you have a new file (ex12_3.tab) in the Perple_X folder.

You can open the ex12_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 13

Ex. 13 – Modelling MELT FRACTIONATION (NKCFMASH system)

This exercise illustrates MELT FRACTIONATION CALCULATIONS for the same system investigated in Exercise 12. 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 150 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. 12.

(1) Definition of the problem (BUILD)

C:\PERPLEX\Perplex715>build

Perple_X release 7.1.5, Dec 1, 2023.
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NO is the default (blank) answer to all Y/N prompts

Enter a name for this project (the name will be used as the root for all output file names) [default = my_project]:
ex13

The problem definition file will be named: ex12.dat

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

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

Reading Perple_X options from: perplex_option.dat

The current data base components are:
Na2O MgO Al2O3 SiO2 K2O CaO TiO2 MnO   FeO   NiO   ZrO2 Cl2 O2 H2O CO2 CuO Cr2O3 S2 F2 N2 ZnO
Transform them (Y/N)?
n

Specify computational mode:
    1 - Convex-Hull minimization
    2 - Constrained minimization on a 2d grid [default]
    3 - Constrained minimization on a 1d grid
    4 - Output pseudocompound data
    5 - 1-d Phase fractionation
    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. 12.

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
Because the thermodynamic data file identifies: H2O as special components, you will be prompted next for the EoS to be used for the corresponding composants and mixtures thereof. To override this behavior, e.g., to use a generic hybrid fluid EoS (GFSM) either:
  set/add the GFSM option to T in your option file
  or delete the special_component section from the thermodynamic data file header.

Select fluid equation of state:
  0 - X(CO2) H2O-CO2 Modified Redlich-Kwong (MRK) DeSantis et al 74
  1 - X(CO2) H2O-CO2 HSMRK Kerrick & Jacobs 81
  2 - X(CO2) H2O-CO2 MRK hybrid-EoS*
  5 - X(CO2) H2O-CO2 CORK Holland & Powell 91, 98
  8 - f(O2/CO2) C-buffered COH MRK hybrid-EoS*
 10 - X(O) C-buffered COH MRK hybrid-EoS Connolly & Cesare 93*
 12 - X(O)-f(S2) C-buffered COHS MRK hybrid-EoS Connolly & Cesare 93*
 13 - X(H2) H2O-H2 MRK hybrid-EoS*
 14 - X(CO2) H2O-CO2 Pitzer & Sterner 94; Holland & Powell mixing 03
 15 - X(H2) H2O-H2 low T MRK hybrid-EoS*
 16 - X(O) H-O MRK hybrid-EoS*
 17 - X(O)-f(S2) H-O-S MRK hybrid-EoS*
 19 - X(O)-X(S) C-buffered COHS MRK hybrid-EoS Connolly & Cesare 93*
 20 - X(O)-X(C) COHS MRK hybrid-EoS Connolly & Cesare 93*
 24 - f(O2/CO2)-N/C C-buffered COHN MRK hybrid-EoS*
 25 - X(CO2)-X(NaCl) H2O-CO2-NaCl Aranovich et al 10
 26 - X(O) O-Si MRK Connolly 16
 27 - X(O)-X(C) C-O-H MRK hybrid-EoS*
*Hybrid EoS use the following pure species EoS, to change these associations modify the hybrid_EoS keywords in the perplex_option file:
    H2O - PSEoS Pitzer & Sterner 1994
    CO2 - PSEoS Pitzer & Sterner 1994
    CH4 - MRK DeSantis et al 1974
5

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
$Y = c_0 + c_1 X_1 + c_2 X_2 + ... + c_n X_n$
where Y is the dependent path variable, X is the independent path variable, c_0 ... c_n 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 c_0 = -5306.67, C_1 = 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 150 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:
 Na_2O MgO Al_2O_3 SiO_2 K_2O CaO   FeO H_2O
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
warning ver056 the EoS specified for H2O   by the hybrid_EoS option will be overridden by the EoS specified in the problem definition file. To prevent this behavior set the GFSM option to True.

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 see:www.perplex.ethz.ch/perplex_solution_model_glossary.html or read the commentary in the solution model file.
Bi(W)
Mica(W)
Gt(W)
St(W)
Crd(W)
Opx(W)
feldspar
melt(W)

Enter calculation title:
Ex13

(2) Doing the calculation (VERTEX)

Run VERTEX to make the calculation:

C:\PERPLEX\Perplex715>vertex

Perple_X release 7.1.5, Dec 1, 2023.
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Enter the project name (the name assigned in BUILD) [default = my_project]:
ex13

…

** 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: ex13_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)   = 950.436   P(bar) = 7362.64
melt(W)   is not stable.
Along the first part of the path, melt is not stable.

At T(K)   = 959.923   P(bar) = 7489.10
melt(W)   is stable, but its mass fraction (0.016) 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:
  6.66000   3.64000   8.95000   70.0900   2.87000   0.280000   6.93000   0.570000
fractionating 4.42173   moles of melt(W) ; will change bulk by:
  2.68359   0.721405E-02 0.678325   5.61380   0.283395   0.287874E-01 0.183878E-01 0.304757
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:
 4.14185   3.63323   8.31349   64.8223   2.60408   0.252987   6.91275   0.284031
fractionating 4.55890   moles of melt(W)   ; will change bulk by:
 2.66613   0.936363E-02 0.706103   6.18538   0.448935   0.326465E-01 0.217090E-01 0.140506

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)   = 1035.82   P(bar) = 8500.82
current molar bulk composition is:
 10.2524   12.7057   27.5740   8.40829   0.839957   23.6537   0.703534
fractionating 7.18596   moles of melt(W)   ; will change bulk by:
 4.20132   0.147342E-01 1.11471   0.708174   0.537317E-01 0.340373E-01 0.220377

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)
    39 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: 128

** 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: ex13_melt(W).dat

At T(K)   = 903.000   P(bar) = 6730.32
melt(W)   is not stable.
…
…
At T(K)   = 957.631   P(bar) = 7458.55
melt(W)   is not stable.

At T(K)   = 960.114   P(bar) = 7491.65
melt(W)   is stable, but its mass fraction (0.016) is below or at the upper fractionation threshold (0.060).
…
…
At T(K)   = 997.362   P(bar) = 7988.17
melt(W)   is stable, but its mass fraction (0.058) is below or at the upper fractionation threshold (0.060).

At T(K)   = 999.846   P(bar) = 8021.27
current molar bulk composition is:
  6.66000   3.64000   8.95000   70.0900   2.87000   0.280000   6.93000   0.570000
fractionating 3.60422   moles of melt(W)   ; will change bulk by:
  2.20562   0.541274E-02 0.546993   4.51273   0.214162   0.219563E-01 0.147924E-01 0.266033

At T(K)   = 1002.33   P(bar) = 8054.37
melt(W)   is stable, but its mass fraction (0.012) is below or at the upper fractionation threshold (0.060).
…
…
At T(K)   = 1027.16   P(bar) = 8385.39
melt(W)   is stable, but its mass fraction (0.056) is below or at the upper fractionation threshold (0.060).

At T(K)   = 1029.64   P(bar) = 8418.49
current molar bulk composition is:
  4.62313   3.63500   8.44486   65.9225   2.67222   0.259724   6.91634   0.324320
fractionating 3.39277   moles of melt(W)   ; will change bulk by:
  2.00424   0.671685E-02 0.526535   4.52014   0.297436   0.242300E-01 0.154667E-01 0.144475

At T(K)   = 1032.13   P(bar) = 8451.59
melt(W)   is stable, but its mass fraction (0.015) 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)   = 1039.58   P(bar) = 8550.89
current molar bulk composition is:
  2.76467   3.62877   7.95662   61.7312   2.39642   0.237256   6.90200   0.190354
fractionating 3.14493   moles of melt(W)   ; will change bulk by:
  1.82586   0.658203E-02 0.487581   4.31967   0.331615   0.226888E-01 0.153099E-01 0.742809E-01

At T(K)   = 1042.06   P(bar) = 8584.00
melt(W)   is stable, but its mass fraction (0.017) is below or at the upper fractionation threshold (0.060).
…
…

At T(K)   = 1119.04   P(bar) = 9610.14

melt(W)   is stable, but its mass fraction (0.059) is below or at the upper fractionation threshold (0.060).

At T(K)   = 1121.52   P(bar) = 9643.24

current molar bulk composition is:

  1.06984   3.62266   7.50403   57.7215   2.08861   0.216195   6.88779   0.121404

fractionating 2.15551   moles of melt(W)   ; will change bulk by:

  1.06984   0.796795E-02 0.412500   3.53207   0.304528   0.197052E-01 0.195638E-01 0.319579E-01

At T(K)   = 1124.01   P(bar) = 9676.34

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 (0.011) is below or at the upper fractionation threshold (0.060).

Timing	min.	% of total
Static G calculation	0.52000E-03	0.8
Dynamic G calculation	0.17940E-01	27.0
Static LP	0.26000E-03	0.4
Dynamic LP	0.16640E-01	25.0
Successive QP	0.26520E-01	39.8
Total of above	0.61880E-01	93.0
Total elapsed time	0.66560E-01	100.0

End of job: ex13

----

(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\Perplex715>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
    aqueous_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   [F] T
    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
 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   0.1E+05  [1d4] >0; fraction = 0.1E-02  [1d-2]
Seismic wavespeed computational options:
 seismic_data_file     T        [F] T
 bounds                VRH      [VRH] HS
 vrh/hs_weighting      0.5      [0.5] 0->1
 explicit_bulk_modulus T        [T] F
 poisson_ratio         on       [on] all off; Poisson ratio = 0.35
 seismic_output        som      [some] none all
 poisson_test          F        [F] T
 Tisza_test            F        [F] T
 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

warning ver056 the EoS specified for H2O   by the hybrid_EoS option will be overridden by the EoS specified in
the problem definition file. To prevent this behavior set the GFSM option to True.

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

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.

Data ranges excluding values equal to bad_number (NaN) specified in perplex_option.dat:

	Bio	Mica	Gt	Fsp	Fsp	q	H2O	Melt	sill
min	0.697106E-001	1.70823	5.86514	1.12720	0.567752	40.6668	0.284599	0.701086	0.364675
max	18.3272	23.9211	25.3905	25.1026	4.19880	48.4419	0.545891	9.10808	5.80788

Output has been written to two files:

Output has been written to two files:

   plt format is in file: ex13_1.plt

   1d tab format is in file: ex13_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 (ex13_1.tab) in the Perple_X folder.
You can open the ex13_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.12).

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 14

Ex. 14 – INDIRECT modelling of an anatectic METAPELITE

In Ex. 12 we have considered a model metapelite, and we have supposed to know the protolith bulk composition (including its initial H_2O amount). However, **in most cases, we have to deal with natural samples, of which we do not know the whole history.** Furthermore, **a number of evidence are consistent with most migmatites and granulites having lost some to virtually all of their melt during metamorphism** (see also Ex. 13)**.**

This exercise aims at modelling a REAL SAMPLE OF ANATECTIC METAPELITE.

What do we know?	**What we do not know?**
• The observed mineral assemblage	• The bulk composition of the protolith (if a certain amount of melt was lost during the prograde evolution)
• The measured mineral compositions	• The amount of melt that was lost
• The measured bulk composition (which generally does not coincide with the composition of the protolith!)	• The number of melt loss events
	• The P-T conditions at which melt was lost

STRATEGY

The problem can be divided in two parts:

(A) If a certain amount of melt was lost during the prograde evolution, the measured bulk composition of the sample represents the FINAL rock composition, after the loss of that melt. Therefore, the pseudosection calculated using the **MEASURED bulk composition** allows to constrain the **P-T evolution from peak conditions to final melt crystallization (i.e. retrograde evolution)**, but may not be valid for the prograde evolution of the rock.

(B) An **APPROXIMATE PROTOLITH COMPOSITION** can be calculated by REINTEGRATING melt into the measured rock composition. The pseudosection calculated using the **MELT-REINTEGRATED bulk composition** allows the exploration of the extended supra-*solidus* domain and the assessment of an **APPROXIMATE prograde evolution**.

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. 14.1 – 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.

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

NB: 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\Perplex715>vertex

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

…

(3) Plotting the calculated phase diagram (PSSECT)

Run PSSECT to plot the calculated pseudosection:

C:\PERPLEX\Perplex715>pssect

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

…

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 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	H2O	MgO	Al2O3	SiO2	K2O	CaO	FeO	TiO2	Na2O
Bio	9.41	8.45	2.05	1.30	0.79714	1.27406	0.78189	2.71811	0.50000	0.00000	1.24119	0.20286	0.00000
Gt	5.28	3.53	1.12	0.713	0.00000	0.72613	1.00000	3.00000	0.00000	0.07867	2.19521	0.00000	0.00000
Fsp	14.46	14.97	5.42	3.45	0.00000	0.00000	0.64072	2.71855	0.03953	0.28145	0.00000	0.00000	0.31974
Fsp	14.15	15.08	5.18	3.30	0.00000	0.00000	0.51248	2.97503	0.36734	0.02497	0.00000	0.00000	0.12017
sill	7.51	6.31	4.66	2.97	0.00000	0.00000	1.00000	1.00000	0.00000	0.00000	0.00000	0.00000	0.00000
q	48.47	51.24	81.09	51.6	0.00000	0.00000	0.00000	1.00000	0.00000	0.00000	0.00000	0.00000	0.00000
ilm	0.72	0.42	0.48	0.305	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	1.00000	1.00000	0.00000

	Mineral modes	
	780°C, 6.6 kbar	
	observed	modelled
Qtz	51.7	48.5
Kfs	14.3	14.2
Sil	5.1	7.5
Bt	9.2	9.4
Grt	4.8	5.3
Pl	14.7	14.5

Ex. 14.2 – 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 H₂O-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 (<ins>better if you extend the T range down to 650°C</ins>); check if the modelled *solidus* is still dry or wet.
- repeat this process until a H₂O-saturated (wet) *solidus* is modelled in the P-range of interest.

(ii) Of which composition?
The composition of reintegrated melt can be calculated at peak-T conditions.

How to estimate the melt composition to be reintegrated?
Run WERAMI, option 1, at peak P-T conditions. The melt composition is expressed in molar proportions of oxides (see below).

Run Werami, option 1 **to estimate the melt composition at peak T conditions** (780°C, 9.0 kbar)

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

Phase Compositions (molar proportions):

	wt %	vol %	mol %	mol	H2O	MgO	Al2O3	SiO2	K2O	CaO	FeO	TiO2	Na2O
Bio	5.71	5.18	1.28	0.800	0.79638	1.42708	0.78082	2.71918	0.50000	0.00000	1.08847	0.20362	0.00000
Gt	9.30	6.30	2.02	1.27	0.00000	0.81888	1.00000	3.00000	0.00000	0.11504	2.06608	0.00000	0.00000
Fsp	13.18	13.68	5.02	3.15	0.00000	0.00000	0.63649	2.72703	0.04196	0.27297	0.00000	0.00000	0.32155
Fsp	16.31	17.42	6.06	3.80	0.00000	0.00000	0.51272	2.97456	0.37243	0.02544	0.00000	0.00000	0.11485
Melt	**1.40**	**1.74**	**1.14**	**0.717**	**0.56153**	**0.00226**	**0.17774**	**1.40423**	**0.07353**	**0.01221**	**0.00595**	**0.00000**	**0.07215**
sill	6.66	5.62	4.19	2.63	0.00000	0.00000	1.00000	1.00000	0.00000	0.00000	0.00000	0.00000	0.00000
q	46.92	49.73	79.64	50.0	0.00000	0.00000	0.00000	1.00000	0.00000	0.00000	0.00000	0.00000	0.00000
ru	0.51	0.33	0.65	0.407	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	1.00000	0.00000

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

	melt composition (790°C, 9.0 kbar)		BC**	Melt reintegrated bulk compositions							
	mol*	mol%	mol%	+ 0.05 mol%		+ 0.10 mol%		+ 0.15 mol%		+ 0.20 mol%	
SiO2	1.4042	60.80	79.45	82.5	78.61	85.5	77.80	88.6	77.06	91.6	76.38
TiO2	0.0000	0.00	0.57	0.6	0.54	0.6	0.52	0.6	0.50	0.6	0.48
Al2O3	0.1777	7.70	8.60	9.0	8.56	9.4	8.52	9.8	8.49	10.1	8.45
FeO	0.0060	0.26	3.49	3.5	3.34	3.5	3.20	3.5	3.07	3.5	2.95
MgO	0.0023	0.10	2.18	2.2	2.08	2.2	1.99	2.2	1.91	2.2	1.83
CaO	0.0122	0.53	1.11	1.1	1.08	1.2	1.06	1.2	1.03	1.2	1.01
Na2O	0.0722	3.12	1.50	1.7	1.58	1.8	1.65	2.0	1.71	2.1	1.77
K2O	0.0735	3.18	2.00	2.2	2.06	2.3	2.11	2.5	2.16	2.6	2.20
H2O	0.5615	24.31	1.04	2.3	2.15	3.5	3.16	4.7	4.08	5.9	4.92
Total	2.3096	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).