PeRpLeX: A Tutorial

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Chapter 1

INTRODUCTION

PeRpLeX is a collection of programs for calculating phase diagrams and equilibria. The purpose of this document is to provide a tutorial for PeRpLeX users through a series of documented examples. This tutorial also discusses some aspects of phase diagram interpretation, but a basic knowledge of thermodynamics is assumed. To calculate a phase diagram with PeRpLeX the first step is to run the program BUILD to create the input file describing the calculation (Fig 1.1 illustrates the structure of PeRpLeX). This file is then read by the program VERTEX which does the phase diagram calculation and outputs summaries of the calculation for printing (the "print" file) and plotting (the "plot" file). Usually the plot file output generated by VERTEX is converted to PostScript with the program PSVDRAW and plotted with a laser printer or edited with a PostScript graphical editor. In each example presented here, the prompts given by BUILD, features of the output from VERTEX, and the uses of PSVDRAW are explained. The examples are progressive, i.e., an understanding of features which are explained in earlier examples is taken for granted in subsequent examples. `Courier` and boldface **`Courier`** fonts are used to distinguish computer output and user responses, respectively, from explanatory commentary. The PeRpLeX program documentation provides detailed information on the thermodynamic equations of state and file structure for the PeRpLeX programs, references to this documentation are written Doc Sect X.X, whereas references to sections within this tutorial are written Tut Sect X.X. In a few cases I have also referenced the `README` and sample problem (in the directory `examples`) files that are included with PeRpLeX. I have tried to use a lot of section headings, so that if you have a specific problem you can use the table of contents as an index. For information on compiling, graphics, etc. refer to the `README` files.

1.1 A Quick and Dirty PeRpLeX Program Glossary

Programs marked by an asterisk are not normally supplied with PeRpLeX, but are available upon request.

ABARTEX*: computes phase diagrams as a function of the composition (or species activities) of graphite undersaturated C-O-H-S fluids (Connolly 1994).

ACTCOR: makes fixed activity corrections for end-member phases in the thermodynamic data file.

ADIABAT*: converts a Gibb’s function thermodynamic data file to an Enthalpy function data file, used to make entropy or enthalpy into a thermodynamic component. Necessary for calculations of polythermal projections and for adiabatic systems (Connolly 1990).

BUILD: reads computational options for calculations with ABARTEX, TERTEX, or VERTEX.

CTRANSF: transforms chemical components in a thermodynamic data file.

COHSRK: calculates fluid properties (and speciation where appropriate) as a function of P, T, X^f_{CO2}, f_{O2}, f_{S2}, X^f_O, etc. (see README.COHSRK).

FRENDLY: general thermodynamic calculator.

HPTOVER*: converts a Holland & Powell (1990) THERMOCALC thermodynamic data file to a PeRpLeX data file.

INPUT9*: reads solution models to test for errors.

ISO: computes isochores of COHS fluids assuming either equilibrium speciation, or constant speciation (see README.ISO).

ISOKOR: converts a Gibb's function thermodynamic data file to an Helmholz function data file, used to make volume into a thermodynamic component. Necessary for calculations of polybaric projections and for isochoric systems (Connolly 1990).

PSCONTOR*: produces PostScript contoured plots of tabulated data output by SPECIES or FRENDLY as a function of two user specified variables.

PSVDRAW: produces PostScript plots of output from SPECIES, FRENDLY, VERTEX, ABARTEX, ISOCOH, and TERTEX.

SPECIES: calculates fluid properties (and speciation where appropriate) as a function of P, T, f_{O2}, f_{S2}, X_O^f, etc. (see README.SPECIES).

STOICH*: calculates all possible singular equilibria involving a binary solution and a set of stoichiometric compounds (see Tut Sect 8).

SUPTOVER*: converts a SUPCRT thermodynamic data file (e.g., Helgeson et al. 1978) to a PeRpLeX data file.

TERTEX*: a modified version of VERTEX for fixed bulk composition calculations (see Tut Sect 9).

UBCTOVER*: converts a UBC/Berman (1988) thermodynamic data file to a PeRpLeX data file.

VERTEX: general phase diagram calculator (Connolly 1990, Connolly & Kerrick 1987).

XOXC*: converts bulk fluid composition coordinates to species compositional coordinates (Connolly 1994).

1.2 Other PeRpLeX Help

In addition to the README files (read them first!), this tutorial, the Review of Phase Diagram Principles, and the PeRpLeX Program Documentation, there are a series of documented examples which may be useful as computational templates. These examples are usually in a folder/directory named `examples` that includes the following files. (Files with a '.ps' suffix are usually supplied as plotted output or are present in the directory special). As with this tutorial, these examples are progressive, i.e., explanations given in earlier examples are not repeated.

sample.1: calculation of a T-X_{CO2} Schreinemakers diagram (figure included with documentation).

in1.dat: input file generated in sample.1 for VERTEX by BUILD (provided as a test for VERTEX).

print1.out: print file generated in sample.1 by VERTEX.

plot1.out: plot file generated in sample.1 by VERTEX (provided as a test for PSVDRAW).

plot1.out.ps: PostScript plot for sample.1.

sample.2: calculation of a ternary AFM ($KAlO_2$ projection) composition diagrams with mineral solutions for a system saturated with respect to a graphite-saturated COH fluid.

in2.dat: input file generated in session.2 for VERTEX by BUILD.

print2.out: print file generated in session.1 by VERTEX.

plot2.out.ps: PostScript plot for sample.2.

sample.3: calculation of a P-T Schreinemakers diagram for a system with mineral solutions and several saturation constraints.

in3.dat: input file generated in session.3 for VERTEX by BUILD.

print3.out: the print file generated in session.3 by VERTEX.

plot3a.out.ps and plot3a.out.ps: PostScript plots for sample.3.

in4.dat: an input file for VERTEX similar to that generated in session.2, run VERTEX with this file to see the effects of changing the component saturation hierarchy in session.2 (see comments in session.2).

sample.5: example illustrating the component transformations necessary to calculate classical J.B. Thompson AFM projections.

in5.dat: input file generated in session.5 for VERTEX by BUILD.

sample.6: calculation of a T-μ_{SiO2} Shreinemakers diagram. demonstrates the use of chemical potentials as independent variables. This session also demonstrates an application of FRENDLY, and provides a relatively simple example of pseudounivariant mineral equilibria.

in6.dat: the input file generated in session.6 for VERTEX by BUILD.

sample.7: calculation of μ_{O2}–μ_{S2} Schreinemakers diagram for the Cu-Fe-Ni system. Illustrates the use of component transformations to obtain elemental components and the use of FRENDLY.

in7.dat: input file generated in session.7 for VERTEX by BUILD.

sample.8: calculation of a Schreinemakers P-T projection for the mixed volatile system CaO-MgO-SiO_2-H_2O-CO_2 for a fluid of variable composition (Connolly & Trommsdorff 1991 and Tut Sect 7).

in8.dat: input file generated in session.8 for VERTEX by BUILD.

in9.dat: input file used for the calculation of plot9, a mixed-variable (T-X_{Mg}) diagram for the AFM system after projection through the aluminosilicate phase.

plot9.out.ps: PostScript plot from in9.dat.

in10.dat: input file to generate a mixed-variable (T-X_{CaO}) diagram for the supersolidus CaO-SiO_2 system.

plot10.out.ps: PostScript plot from in10.dat.

sample.11: calculation of a T-X_O^f diagram for the graphite+fluid+quartz+ aluminosilicate saturated system CaO-FeO-Al_2O_3-SiO_2-C-O-H-S where f_{S2} constrained by pyrrhotite composition (Connolly & Cesare 1993, Connolly 1994).

plot11.out.ps: PostScript plot from in11.dat.

1.3 Help for Solution Models

Invariably the biggest problem users have with PeRpLeX is using, modifying, and creating solution models. For modifying solution models see Fig 4.1, Doc Sects 4 & 1.4, and Tut Sect 7.2. For creating solution models see Doc Sects 1 & 4. For interpreting solution models see Tut Sects 4, 5 & 7, the review of phase diagram principles, and the example problems.

Chapter 2

A SIMPLE COMPOSITION PHASE DIAGRAM

The most basic type of phase diagram that can be calculated with VERTEX is the composition phase diagram. A composition phase diagram is a diagram which shows the phase relations of a system as a function of its independent compositional variables with all the other variables (usually P, T, and the chemical potentials of constrained components) held constant. AFM and ACF diagrams are examples of composition phase diagrams that are common in petrologic analysis. In petrologic jargon such diagrams are often called chemographic diagrams, or simply chemographies. This example illustrates the calculation of a composition phase diagram for the system $MgO–K_2O–SiO_2–Al_2O_3–H_2O–CO_2$ a system saturated with respect to silica and a binary $H_2O–CO_2$ fluid. The first step is to run BUILD, the user receives the following prompts and makes the indicated responses:

2.1 File Locations and Names.

```
Enter the name of the computational option file to be created, left justified,
<15 characters:
in.dat
```

This will be the name of the computational option file (Doc Sect 2) written by BUILD and later read by VERTEX. PeRpLeX does not require any particular format for file names; however, certain operating systems may have some restrictions. Most IBM machines use a filename.filetype format where filename must be less than 9 characters, and filetype must be less than 3 characters, DEC machines (VAX, PDP) running VMS also have this format without any limit on the length of filename. In most cases, for these machines if the filetype suffix is not supplied a "dat" suffix is added automatically, e.g., if the user responded to the above prompt with **`in`** the file would be written to `in.dat.` For UNIX and MacIntosh computers there is no specific filename format.

In principle, it is possible to give directory specifications with the file name in response to a PeRpLeX prompt; however, as the total number of characters must be less than 15 this is generally not possible. Consequently, files used by the PeRpLeX programs must be located in the directory where the user is working.

```
Enter thermodynamic data file name (e.g. hp94ver.dat), left justified:
hp94ver.dat
```

This is the name of the thermodynamic data file (Doc Sect 3), which contains the standard state data for compounds and species. A PeRpLeX thermodynamic data file may contain several thermodynamic databases, in which case the user is asked to choose one. The file `hp94ver.dat` contains only a version of the data base created by Holland and Powell (1989). Most of the names of most thermodynamic data files end in "ver.dat." The integrity of the data files supplied with PeRpLeX is not guaranteed, and for important calculations the data should be verified.

```
Do you want to a print file (Y/N)?
y
Long print file format (Y/N)?
n
```

```
Do you want to a graphics file (Y/N)?
y
Enter print file name, <15 characters, left justified:
print.dat
Enter graphics file name, <15 characters, left justified:
plot.dat
```

Whether VERTEX generates print and/or graphics file is optional, the previous prompts determine the names of these files. The print file format question has no effect on the output for composition diagrams.

```
Specify type of calculation:
0 - Composition diagram
1 - Schreinemakers diagram
3 - Mixed-variable diagram
0
```

2.2 Printing the Dependent Potentials

```
Print dependent potentials for chemographies (Y/N)?
n
```

The user has the option of printing the potentials (usually chemical potentials) of the thermodynamic components (discussed below) in every phase assemblage of the composition phase diagram. For most purposes this option is unnecessary. When this option is requested the potentials are printed in the same order the thermodynamic components are entered, and follow the list of phase assemblages.

2.3 The Composition Space

```
The data base components are:
NA2O  MGO   AL2O3 SIO2  K2O   CAO   TIO2  MNO   FEO   O2    H2O   CO2
Transform them (Y/N)?
n
```

VERTEX calculates phase relations within the composition space spanned by a positive linear combination of the thermodynamic components, or a subset thereof, defined in the thermodynamic data file (Doc Sect 3). Because phases outside this composition space (i.e., phases with negative compositional variables) are not considered, for a calculation to be valid the composition space must be a true thermodynamic join, i.e., none of the phase relations within the composition space may become metastable with respect to a phase outside the composition space. For example, if the components are CaO-Al_2O_3–SiO_2, the composition space is the triangular region outlined in Fig 2.1. Alternatively, the components might be chosen as $CaSiO_3$–Al_2O_3–SiO_2, in which case the composition space is the region outlined by dashed lines in Fig 2.1. Considering the compound phases wo, geh, an, gr, lime, cor, sil, and q, the CaO-Al_2O_3–SiO_2 composition space is valid for all conditions, but the $CaSiO_3$–Al_2O_3–SiO_2 composition space is only valid if there are no tielines crossing the line connecting wo and cor. However, provided the $CaSiO_3$–Al_2O_3–SiO_2 composition space is valid, then it may be more convenient to work with because it has simpler phase relations.

The foregoing prompt lists the thermodynamic data file components, and permits the user the option of changing them for the calculation. An example where this is done is presented in Tut Sect 3. Most of the thermodynamic data files are based on simple oxide components and for most geologic purposes these components define valid, although not always optimal, composition spaces.

2.4 Saturation Constraints

```
Calculations with a saturated phase (Y/N)?
The phase is:   FLUID
Its components can be: H2O   CO2
Its compositional variable is: X(CO2)
y
Enter the number of components in the   FLUID
(1 or 2 for COH buffered fluids):
2
Calculations with saturated components (Y/N)?
y
Select saturated components from the following set:
NA2O  MGO   AL2O3 SIO2  K2O   CAO   TIO2  MNO   FEO   O2
How many saturated components (maximum 5)?
1
Enter component names, left justified, one per line:
SIO2
```

In many petrologic problems the analysis of phase relations can be greatly simplified if it is known, or assumed, that certain phases are stable, i.e., saturated, at all the conditions of interest. In petrologic jargon, the phase relations are said to be projected through the saturated or "excess" phases. In VERTEX such constraints may be implemented in one of two ways, distinguished as "phase" and "component" saturation. In the present problem the constraints that silica and an H_2O–CO_2 fluid of known composition are present in excess correspond, respectively, to component and phase saturation constraints. Components which are effected by saturation constraints are not considered to be thermodynamic components, i.e., the composition space is projected through the constrained components to obtain a thermodynamic composition space with fewer components.

2.4.1 Phase Saturation

Phase saturation constraints are implemented with the assumption that the specified phase is stable and no test of the validity of this assumption is made. For example, if fluid phase saturation is specified no tests are made to determine if the fluid is miscible, or if the fluid speciation is consistent with other constraints such as externally imposed μ_{O2}. The components of the saturated phases are eliminated from the thermodynamic composition space. In the present problem, the specification that the system is saturated with respect to an H_2O–CO_2 fluid reduces the thermodynamic composition space from MgO–K_2O–SiO_2–Al_2O_3–H_2O–CO_2 to MgO–K_2O–SiO_2–Al_2O_3. If a saturated phase has more than two components then its compositional variables are independent variables for the computation. Thus, if a phase diagram is to be calculated as a function of X^f_{CO2}, then the fluid phase saturation option, and both fluid components (H_2O–CO_2), must be chosen. If a phase diagram is to be calculated with the assumption $P_{H2O}=P_{total}$, fluid phase saturation must also be specified, but only the H_2O component chosen.

At present, only one phase saturation constraint is permitted in a calculation, although this is not an algorithmic limitation. The identity of the saturated phase and its components are specified in the thermodynamic data file and can be changed (Doc Sect 3); however the addition of new saturated phases (e.g., feldspar) requires some modification of the PeRpLeX sources (Doc Sect 1.8). All the data files provided with PeRpLeX are configured for unary or binary H_2O–CO_2 fluids, and graphite-saturated C-O-H-S fluids (the latter are treated as a special case by BUILD, Tut Sect 6).

2.4.2 Component Saturation

In contrast to phase saturation constraints, where the identity of the saturated phase is specified, for component saturation constraints the identities of components are specified and the saturated phases with the corresponding compositions are determined. Component saturation constraints are implemented after phase saturation constraints; thus if H_2O-CO_2 fluid-phase-saturation has been imposed, and CaO were chosen as a saturated component, then the corresponding saturated phase might be calcite, lime, or portlandite depending on the fluid composition and P-T conditions. Each component saturation constraint eliminates one component from the thermodynamic composition space. In the present problem, the specification of silica as a saturated component means that at any condition the stable silica polymorph (quartz, β–quartz, coesite, etc.) will be chosen as the saturated phase, and the thermodynamic composition space will be the ternary $MgO-K_2O-Al_2O_3$ (i.e., all phase relations will be "projected through" H_2O, CO_2, and SiO_2).

In general, if a given mineral (or polymorph) is present throughout a petrologic sequence it can be represented by a component saturation constraint. However there is one important restriction on this, namely that if a phase can be represented by a component saturation constraint its composition (after whatever other constraints imposed have been applied) must correspond to a valid component (Tur Sect 2.3). If the mineral is a complex oxide it is usually necessary to redefine the thermodynamic components (as defined in the thermodynamic data file) to provide a component with the same composition as the mineral. For example consider rocks represented by the system shown in Fig 2.1, assuming wollastonite is always stable. As noted earlier, for wollastonite composition to be a valid component no tielines may cross the wo + co join. If this is true and $CaSiO_3$ taken as a saturated component, then either CaO and Al_2O_3, or Al_2O_3 and SiO_2 may be chosen as the remaining thermodynamic components depending on which side of the composition space, relative to the wo + co join, is of interest. Note that if phases on both sides of the wo + co join are observed then it would be necessary to do calculations for both systems separately.

It is possible to specify up to six component saturation constraints for a calculation. Multiple component saturation constraints are applied hierarchically with the result that it is possible to represent complex saturation sequences (Tut Sect 3).

2.4.3 Buffered Components

Saturated component constraints are evaluated determining the thermodynamic entity that yields the lowest chemical potential for the component in question. Normally such entities are phases, but they may also be a fictive entity that has the chemical potential appropriate for a buffer equilibria (Doc Sect 6). For example, such fictitious entities are useful in calculations where μ_{O2} is assumed to be a known function of P and T.

2.5 Chemical Potentials as Independent Variables

```
Use chemical potentials as independent variables (Y/N)?
n
```

This option permits the user to compute diagrams with the potentials of the thermodynamic components on one or more phase diagram axes (Tut Sect 10 and files Sample.6 and Sample.7), or a composition phase diagram with one or two fixed potentials (in addition to those fixed by saturation constraints). If a potential is chosen an independent variable, the corresponding component is eliminated from the thermodynamic composition space.

2.6 Thermodynamic Components

```
Select thermodynamic components from set:
NA2O  MGO   AL2O3 K2O   CAO   TIO2  MNO   FEO   O2
How many thermodynamic components (<7)?
3
Enter component names, left justified, one per line:
MGO
K2O
AL2O3
```

The components selected in response to this prompt will be the c thermodynamic components for the phase diagram calculation.

2.7 Constrained Bulk Compositions

```
Constrained bulk compositions (y/n)?
n
```

Normally PeRpLeX computes phase relations over the entire composition space of the system spanned by the thermodynamic components. However in some cases it may be desired to compute phase relations that would be observed for a specific bulk composition, this option (Tut Sect 8, and file `README`) permits such calculations.

2.8 Equations of State for H_2O-CO_2 Fluids

```
Select fluid equation of state:
  0 - X(CO2) Modified Redlich-Kwong (MRK/DeSantis/Holloway)
  1 - X(CO2) Kerrick & Jacobs 1981 (HSMRK)
  2 - X(CO2) Hybrid MRK/HSMRK
  3 - X(CO2) Saxena & Fei 1987 pseudo-virial expansion
  4 - Bottinga & Richet 1981 (CO2 RK)
  5 - X(CO2) Holland & Powell 1991 (CORK)
  6 - X(CO2) Hybrid Haar et al 1979/HSMRK (TRKMRK)
  7 - f(O2/CO2)-f(S2) Graphite buffered COHS MRK fluid
  8 - f(O2/CO2)-f(S2) Graphite buffered COHS hybrid-EoS flui
  9 - Max X(H2O) GCOH fluid Cesare & Connolly 1993
 10 - X(O) GCOH-fluid hybrid-EoS Connolly & Cesare 1993
 11 - X(O) GCOH-fluid MRK Connolly & Cesare 1993
 12 - X(O)-f(S2) GCOHS-fluid hybrid-EoS Connolly & Cesare 19
 13 - X(H2) H2-H2O hybrid-EoS
 14 - EoS Birch & Feeblebop (1993)
 15 - X(H2) low T H2-H2O hybrid-EoS
 16 - X(O) H-O HSMRK/MRK hybrid-EoS
 17 - X(O) H-O-S HSMRK/MRK hybrid-EoS
 18 - X(CO2) Delany/HSMRK/MRK hybrid-EoS, for P > 10 kb
 19 - X(O)-X(S) COHS hybrid-EoS Connolly & Cesare 1993
 20 - X(O)-X(C) COHS hybrid-EoS Connolly & Cesare 1993
5
```

The foregoing prompt is issued if either of the special (fluid) phase components (usually H_2O or CO_2) are entered in response to the prompts for saturation constraints or thermodynamic components (Tut Sect 7). Of the equations of state listed choices 0, 1, 2, 3, 5, 6, and 18 are valid for binary or unary H_2O-CO_2 fluids. Choice 4 is valid only for CO_2 fluids. Most thermodynamic data bases are based on equilibria which involve a fluid phase, and are therefore derived with a specific fluid equation of state. When using such data bases it is usually wise to choose (if possible) the fluid equation of state used in the data derivation for calculations. Thus, the Holland and Powell (1991) equation of state is optimal for the Holland and Powell (1990) data base; and Kerrick and Jacobs' (1981) equation of state (or the hybrid equations of state, choices 2, 6 or 18) for Berman's (1988) data base. At P-T conditions near the H_2O-CO_2 solvus these equations of state fail, in which case the MRK (choice 0) is useful, the MRK is an equation of state proposed by DeSantis (1974) with some parameters from Connolly (1981). At high pressures above 20 kbar most of the equations of state for water become thermodynamically unrealistic, CORK (choice 5) and the hybrid equation (choice 18) based on Delany & Helgeson's water equation of state (1984) minimizes this problem. For rough calculations the differences between the equations of state are not important and in the interest of saving computer time choices 5 and 0 are optimal. Choices 7-17 are equations of state for multispecies H-O, H-O-S, C-O-H and C-O-H-S fluids (Tut Sect 6). See the file `README.COHSRK` for the most up-to-date description of PeRpLeX fluid equations of state.

2.9 Excluding Compound Phases and Fictive Composants

```
Exclude phases (Y/N)?
y
Do you want to be prompted for phases (Y/N)?
y
Exclude k2o      (Y/N)?
n
Exclude sio2     (Y/N)?
y
Exclude al2o3    (Y/N)?
y
Exclude mgo      (Y/N)?
y
Exclude mu       (Y/N)?
n
Exclude ...
```

By default VERTEX does calculations with all the compound phases in the data base with appropriate compositions. Because of the relative efficiency of the program, this does not pose a notable computational burden except on very slow computers. However, it is often desirable to simplify computational results by excluding some phases from consideration. If the user elects to exclude compound phases, she has the option of entering the list herself, or, as done here, of being prompted for the appropriate phases. The latter option is sure, but tedious, whereas the former requires familiarity with the compound phase names.

Frequently users exclude so many phases from consideration that their calculations become meaningless. For example, suppose a user has observed the phases staurolite, biotite, quartz, and muscovite; often the user then reasons that since he does not observe garnet, chlorite, cordierite, chloritoid, etc. in his rock that these phases are irrelevant and can be excluded. This is flawed reasoning because if these phases are excluded there are virtually no phases remaining with respect to which the observed phases can become metastable.

VERTEX requires that for every component there must be at least one compound (a composant) with the same composition as the component. For many possible components, e.g. K_2O, no true composant exists in the thermodynamic data, but to permit calculations with such components "fictive" composants are included in the data base. The phase relations calculated with a fictive composant do not represent possible phase equilibria, therefore phase diagrams calculated with fictive composants are only valid at those conditions where the fictive composants are not stable. In the PeRpLeX thermodynamic data files, fictive composants are usually near the beginning of the file, and are given the corresponding component name in lower case characters. If components are redefined (Tur Sect 2.3) it is possible that no suitable composant exists for the new component, in which case it is necessary to create a composant as described in Doc Sect 1.6.

In the present example, the compounds k2o, sio2, al2o3, and mgo are fictive composants, of which all but k2o may be excluded because of the true compounds quartz, corundum, and periclase. When in doubt as to whether a composant is necessary or not it is best to allow the composant.

2.10 Solution Phases

```
Consider solution phases (Y/N)?
n
```

This question refers to solution phases other than the saturated fluid phase, examples involving solutions are discussed in Tut Sects 4 & 5.

2.11 Running VERTEX and PSVDRAW

```
Enter a one-line title for your calculation:
A Simple Composition Phase Diagram
How many composition diagrams do you want to calculate?
1
Specify values for :
         P(bars)   T(K)      X(CO2)
For calculation number 1
2000 773 0.5
```

After the foregoing prompts BUILD terminates and writes the file `in.dat.`

2.11.1 VERTEX

The user then runs VERTEX which issues the prompt:

```
Enter computational option file name, left justified:
in.dat
```

and the user messages:

```
Reading thermodynamic data from file: hp94ver.dat
Writing print output to file: print.dat
Writing plot output to file: plot.dat
Reading solution models from file: none requested
```

2.11.2 PSVDRAW Graphics

PSVDRAW can only plot ternary composition phase diagrams (as in the present example). To make such plots the user runs PSVDRAW, with the following dialogue:

```
Enter plot file name:
plot.dat
PostScript will be written to file: plot.dat.ps
```

PSVDRAW creates a name for its output file by appending the suffix ".ps" to the input file name, on some operating systems such three part names may not be permitted (perhaps VMS), in which case a simpler plot file name should be used. The graphics generated from the output file plot.dat.ps are shown in Fig 2.2. Note that in Fig 2.2, there are two phase regions, kf + phl + k2o and ta + phl + k2o, which involve the fictive composant k2o. Consequently only those regions on the aluminous side of the kf + phl + cumm join represent real phase relations. It would have been possible to eliminate the fictive portion of the diagram by defining a component with the composition $KAlO_2$.

2.12 Print File Output

The print file generated by VERTEX for composition phase diagrams consists of two parts, the first part is basically an echo of the users input, and the second summarizes the computational results.

2.12.1 Title Segment

```
Problem title: A Simple Composition Phase Diagram

Thermodynamic data base from: HOLLAND AND POWELL 1989
Fluid equation of state: Holland and Powell 1990 (CORK)

independently constrained potentials:
     P(bars)  T(K)     X(CO2)
saturated phase components:
    H2O      CO2
saturated or buffered components:
    SIO2
components with unconstrained potentials:
    MGO         K2O         AL2O3
```

2.12.1.1 Phase Names and Compositions

The next section of the title segment lists all the phases in the thermodynamic composition space for the calculation (i.e., phases whose stabilities are not determined solely by saturation constraints). Note that the compositions given are the mole fractions of the thermodynamic components (i.e., the compositions after the constrained components have been subtracted from the general composition).

The PeRpLeX programs use abbreviated phase names defined in the thermodynamic data file (Doc Sect 3, Read 1) and in many cases these may be cryptic. Often it is possible to determine the identity of such a phase from its thermodynamic composition, when this is not possible the full composition can be determined from the thermodynamic data file (Doc Sect 3).

```
Phases and (projected) composition with respect to K2O and AL2O3 :
ant    0.00  0.00     k2o    1.00  0.00     al2o3  0.00  1.00
mgo    0.00  0.00     mu     0.25  0.75     cel    0.25  0.25
phl    0.12  0.12     east   0.12  0.38     clin   0.00  0.17
 ...
m(h&p) 0.00  0.00     m(t&c) 0.00  0.00     and    0.00  1.00
ky     0.00  1.00     sill   0.00  1.00     sp     0.00  0.50
mcar   0.00  0.50     per    0.00  0.00     cor    0.00  1.00
```

This section lists those phases whose stabilities are determined entirely by component saturation constraints (in the present case pure silica compounds):

```
phases on saturation and buffering surfaces:
sio2      q         bq        coe
```

This section lists those phases which have been excluded from consideration by the user:

```
excluded phases:
cao       pswo      cz1
```

2.12.2 Computational Results

Composition phase diagrams calculated by VERTEX are described in the print file by listing all the stable phase assemblages of the diagrams for each value of the independent variables. For calculations with three or more thermodynamic components, each assemblage is described by giving the names of the coexisting phases (except for those determined by the saturation constraints) separated by dashes and followed by an integer number in parentheses. This integer number is used to distinguish different types of assemblages in problems with solution phases in the thermodynamic composition space, but is irrelevant in the present problem. Binary composition phase diagrams are described by listing the stable phases in the order that they occur along the binary join in question.

```
the stable assemblages at:
                         P(bars)  =  2000.00
                         T(K)     =  773.000
                         X(CO2)   = 0.500000
are:
ta      -k2o     -phl   (1)         ta      -clin    -phl   (1)
clin    -and     -mu    (1)         k2o     -kf      -phl   (1)
kf      -mu      -phl   (1)         clin    -phl     -mu    (1)
```

Following the list of phase assemblages in the thermodynamic composition space the identities of those phases determined by the component saturation constraints are listed. These phases coexist with all the assemblages in the thermodynamic composition space, as does the saturated (fluid) phase, if specified.

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

Chapter 3

SCHREINEMAKERS DIAGRAMS, COMPONENT TRANSFORMATIONS AND SATURATION HIERARCHIES

Schreinemakers diagrams are by far the most common type of diagram used to represent petrologic phase equilibria. A Schreinemakers diagram is any diagram in which the invariant and univariant phase relations of a multicomponent system are projected onto a two-dimensional potential variable (P, T, μ_i, X^f_{CO2}, X^f_O, f_i, or a_i, etc.) coordinate frame. For simple problems, such as that outlined in the previous chapter, the responses to the prompts given by BUILD that are necessary to calculate a P–T–X^f_{CO2} Schreinemakers diagram should now be evident (the user may wish to verify this for herself). Therefore, this chapter will consider a more complex problem in the fluid-saturated system CaO–MgO–K_2O–Al_2O_3–SiO_2 at P = 2000 bar, T = 673 to 753 K, and X^f_{CO2}= 0 to 1 moles CO2.

It would be straightforward to treat this problem by entering all the components as thermodynamic components, but this would result in a complicated diagram with many equilibria that are irrelevant to most geologic problems. In a given system, if one observes that there is an s-component subsystem in which one component is consistently saturated and there are at least s phases stable in the subsystem, then it is possible to eliminate the s-component subsystem from the thermodynamic composition space by using multiple component saturation constraints. If the total number of components for the system is n, these constraints reduce the thermodynamic composition space to c=n–s components. For calculations with multiple component-saturation constraints, VERTEX computes the phase assemblage in the s-component subsystem at every P–T–X^f_{CO2} condition and then determines the stable phase assemblages in the c-component thermodynamic composition space consistent with the existence of the s-phase assemblage. As an example of this, here the Schreinemakers diagram will be calculated for a system which is always saturated with respect to silica (quartz) and two compound phases in the chemical subsystem K_2O–Al_2O_3–SiO_2, the phase relations of which are shown in Fig 3.1. From Fig 3.1 it can be seen that at low X^f_{CO2}, for more aluminous compositions, the stable phase assemblage is q + mu + and, if temperature is increased eventually mu dehydrates and the stable aluminous silica-saturated assemblage will be q + kf + and. Alternatively, for relatively more potassic compositions at low X^f_{CO2}, the stable silica-saturated assemblage will be q + kf + mu, and q + kf + and at higher $X^{f.}_{CO2}$ The user can control which sequence of saturated phase assemblages will be computed by VERTEX by the order in which the saturated components are specified, i.e., the component saturation hierarchy.

3.1 Component Saturation Hierarchies

The necessity of component saturation hierarchies can be demonstrated by considering what would happen if each saturated component were evaluated independently. For example, suppose that in the K_2O–Al_2O_3–SiO_2 system (after projection through the saturated fluid-phase components) both Al_2O_3 and SiO_2 were chosen as saturated components, then, for the conditions illustrated in Fig 3.1, the saturated-phase assemblage would be q + co, but this assemblage is not stable with respect to aluminosilicate (and), therefore this approach is thermodynamically inconsistent. VERTEX makes use of an alternative approach, in which multiple component saturation constraints are evaluated sequentially, this sequence is the component saturation hierarchy. In the previous example, if the component saturation hierarchy Al_2O_3–SiO_2, is specified, VERTEX will first determine the stable Al_2O_3 compound (co), and then the stable Al_2O_3–SiO_2 compound (and) that coexists with co, this assemblage (or actually the values of

μ_{Al2O3} and μ_{SiO2} determined by the assemblage) is then used to compute the other stable phases in the system. Another way of thinking about this procedure, is that after the stable Al_2O_3 compound is determined, all the Al_2O_3–SiO_2 compounds are be projected into the SiO_2 subsystem, and the phase with the lowest projected free energy taken to represent the SiO_2 saturation constraint. If K_2O was specified as the third saturated component, all the K_2O–Al_2O_3–SiO_2 compounds would then be projected into the K_2O subsystem and the phase with the lowest projected free energy chosen to represent the K_2O saturation constraint, this will be the phase with tielines to co + and at the P–T–X^f_{CO2} condition of interest (either mu or kf in Fig 3.1).

For the calculation proposed in this chapter, it is stipulated that the system is always saturated with respect to silica; thus, silica must be specified as the first component in the saturation hierarchy. If the K_2O–Al_2O_3–SiO_2 phases are now projected onto the K_2O–Al_2O_3 join (Fig 3.2) it can be seen from Fig 3.1 that if Al_2O_3 is chosen as the second saturated component, andalusite will be the Al_2O_3-saturated phase, and either mu or kf will be the K_2O-saturatedphase. Thus, the saturation hierarchy SiO_2–Al_2O_3–K_2O will yield the aluminous series of phase assemblages q + and + mu and q + and + kf. There is a complication in specifying the alternative hierarchy, SiO_2–K_2O–Al_2O_3, namely that there is no true phase with the K_2O composition after projection through SiO_2 (VERTEX would allow such a calculation, but phase relations saturated with respect to a fictive phase are meaningless). Thus, to obtain the potassic series of assemblages it is necessary to redefine the potassic component K_2O as $KAlO_2$. If the saturation hierarchy SiO_2–$KAlO_2$–Al_2O_3 is then specified, for the conditions of interest the saturated-phase assemblages will be q + kf + mu and q + kf + and.

The definition of new components, and their use in VERTEX, can sometimes be very tricky, it is particularly important to remember that a component defined for VERTEX must be a valid thermodynamic component (Tur Sect 2.4). For example, in the present case it would be possible to define KAl_3O_5 as a component to calculate q + mu-saturated phase assemblages, but such calculations would only be valid within the q + mu stability field and VERTEX will not inform the user if this is not the case. Users should always check carefully that the saturated phase assemblages are those desired. Often it is helpful to first make a calculation in the subsystem of the saturated components (as in Fig 3.1 for the present problem) to determine the best approach to a calculation.

3.2 Running BUILD

This section summarizes the output generated by BUILD to do the calculation outlined above, assuming the component saturation hierarchy SiO_2–$KAlO_2$–Al_2O_3. The first few prompts and responses are not shown, these are identical to those in Tut Sect 2.1 with the exception that the user selects the Schreinemakers diagram option (2). The output shown here commences with the print file format prompt (prompts for which the responses are obvious are omitted here).

3.2.1 Print File Format

```
Long print file format (Y/N)?
y
```

If long print file format is requested, as done here, VERTEX outputs the loci of each equilibrium as it is determined. In many cases an equilibrium may be traced many times and as series of overlapping segments. Given that this information is plotted by PSVDRAW, often it is not needed by the user and can be eliminated from the print file by responding `n` to this prompt. If this is done VERTEX writes only problem set-up information and a list of all equilibrium identified. For experienced VERTEX users this information is all that is needed in conjunction with plotted output. For complicated problems use of the short print file form can result in a considerable savings in computer time, disk space, and paper.

3.2.2 Reliability Levels

```
 ...
Specify reliability level [1-5, default is 5]:
  1 - gives lowest efficiency, highest reliability
  5 - gives highest efficiency, lowest reliability
High values increase the probability that a curve
may be only partially determined or skipped entirely.
5
```

One of the drawbacks of the VERTEX algorithm is that VERTEX makes a large number redundant calculations for Schreinemakers diagrams. The problem in attempting to reduce these is that making the program more efficient increases the probability that VERTEX will skip part of a univariant curve. This prompt permits the user to choose the level of reliability for a calculation, usually level 4 or 5 is adequate. With low reliability levels errors most often occur in complex systems with a high degree of compositional degeneracy. Generally such errors are obvious in that they results in lopsided looking invariant points (i.e., a barren sector of more than 180 degrees about an invariant point). Even with the lowest (5) reliability level the probability of an error occurring is small. Should there be any doubts about a Schreinemakers diagram, it can always be checked by computing a mixed-variable diagram section through it, or alternatively composition diagrams can be calculated in suspicious $P\text{–}T\text{–}X^{f}_{CO2}$ regions. The algorithms for both composition and mixed-variable diagrams are completely reliable.

3.2.3 Reaction Equation Format

```
Write full reaction equations (Y/N)?
n
```

By default reaction equations (Tut Sect 3.4.3.1) are written only with the names of phases in the thermodynamic composition space. The stable phases determined by component and phase saturation constraints, and stoichiometric coefficients of the reaction are listed separately. Alternatively a single reaction equation can be written that includes all, or some, of this information.

3.2.4 Console Messages

```
Suppress console status messages (Y/N)?
n
```

Ordinarily VERTEX writes information on the status of a calculation to the users terminal screen (console). This may cause jobs to run more slowly or may interfere with the users other activities. This can be stopped by responding yes to this prompt.

3.2.5 Redefining Components

The following prompts concerns the definition of the $KAlO_2$ component as discussed in Tut Sect 3.1, these prompts are largely self-explanatory. The only exception to this is the choice of the data base component to be replaced by the newly defined component. Because VERTEX determines the amount of the new component in a phase from the amount of the component to be replaced, the amount of the component to be replaced in the new component must be non-zero. In the present case, $KAlO_2$ is defined in terms of two of the data base components, K_2O and Al_2O_3, and therefore only these components may be replaced by $KAlO_2$ however, the Al_2O_3 component is necessary for the calculation, and so the user must replace K_2O.

```
The data base components are now:
NA2O  MGO   AL2O3 SIO2  K2O   CAO   TIO2  MNO   FEO   O2    H2O   CO2
Transform them (Y/N)?
y
Enter the new component name (< 5 characters left justified, blank to finish):
KALO3
Enter the old component you wish to replace with KALO3:
K2O
Enter the other components (<12) in KALO3 one per line, blank to finish:
AL2O3

Enter the stoichiometric coefficients of:
  K2O   AL2O3
in KALO3 (in the above order):
0.5 0.5
KALO3 =   0.50 K2O     0.50 AL2O3
Is this correct (Y/N)?
y
 ...
Calculations with a saturated phase (Y/N)?
The phase is:   FLUID
Its components can be: H2O   CO2
Its compositional variable is: X(CO2)
y
Enter the number of components in the   FLUID
(1 or 2 for COH buffered fluids):
2
Calculations with saturated components (Y/N)?
y
Select saturated components from the following set:
NA2O  MGO   AL2O3 SIO2  KALO3 CAO   TIO2  MNO   FEO   O2
How many saturated components (maximum 5)?
3
Enter component names, left justified, one per line:
SIO2
KALO3
AL2O3
Use chemical potentials as independent variables (Y/N)?
n
Select remaining components from the following set:
NA2O  MGO   CAO   TIO2  MNO   FEO   O2
How many thermodynamic components (<8)?
2
Enter component names, left justified, one per line:
CAO
MGO
Select the fluid equation of state:
   0 - Modified Redlich-Kwong (MRK)
              ....
  18 - Delany/HSMRK/MRK hybrid-EoS, for P > 10 kb
6
Exclude phases (Y/N)?
n
Select x-axis variable:
```

```
          1 - P(bars)
          2 - T(K)
          3 - X(CO2)
3
Enter minimum and maximum values, respectively, for: X(CO2)
0 1
Select y-axis variable:
          2 - T(K)
          3 - P(bars)
2
Enter minimum and maximum values, respectively, for: T(K)
673 873
```

3.2.6 Multiple Sections

```
Calculate sections as a function of a third variable (Y/N)?
n
```

The present calculation will be a single isobaric section, this prompt provides the user with the option of calculating multiple sections. However, PSVDRAW will only plot one section.

```
Specify sectioning value for: P(bars)
2000
Consider solution phases (Y/N)?
n
Enter a one-line title for your calculation:
A Schreinemakers Diagram (CaO-MgO)
```

3.3 Running VERTEX and PSVDRAW

After running BUILD, the user runs VERTEX which prompts for the name of the file created by BUILD, and writes some information on the progress of the calculation. PSVDRAW can then be run to generate a PostScript plot, if the user elects to accept the default plotting options a plot such as that shown in Fig 3.3 is obtained. Wherever possible PSVDRAW attempts to label curves by the associated reaction equation, when this is not possible PSVDRAW identifies the curve by number; points are always labeled by number. The identities of curves and points labeled by number can be determined from the lists given in the print file (Tut Sect 3.4). A peculiarity of diagrams calculated with saturated components is that univariant curves may abruptly change slope, these changes correspond to a change in the saturated-phase assemblage. In Fig 3.3, this occurs for the cc = an and dol = m(h&p) + an (curve 10) curves when the saturated-phase assemblage changes from q + kf + mu to q + kf + and with increasing X^{f}_{CO2}.

3.3.1 Modifying Default Plot Options

The default plot options in PSVDRAW can be modified to effect several features, in particular to control the way in which curves and points or labeled. The following dialogue illustrates some of these features.

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

```
y
Modify default drafting options (y/n)?
y
```

To reduce the number of prompts, two classes of modifications are considered, raw drafting options, and options which effect the kind and identities of the equilibria to be shown.

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

This prompt permits the user the option of plotting only a portion of the diagram.

```
Fit curves with B-splines (y/n)?
y
```

The PSVDRAW default is to smooth curves with B-splines.

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

This option permits the user to suppress all curve labeling.

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

The PSVDRAW default is to label only curve segments that have a length of more than 2% of the axes length, segments that have a length greater than this, but less than 15% of the axes length, receive numeric labels, and segments with a length of greater than 15% of the axes length receive text labels. Note that a univariant curve may consist of several curve segments, and only the first segment identified in the plot file will be labeled.

```
Enter minimum fraction of the axes length that a
curve must be to receive a text label (0-1):
0.2
```

The user specifies that all curve segments > 20% of the axes length will receive text labels.

```
Enter minimum fraction of the axes length that a
curve must be to receive a numeric label (0-0.200):
0.05
```

The user specifies that a curve must exceed 5% of the axes length to be labeled, and therefore by default that curve segments with lengths between 5 and 20% of the axes length will receive numeric labels.

```
Reset default size for text labels (y/n)?
y
Scale default text size by a factor of:
1.2
```

This option only effects the size of the characters used to label curves and points.

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

This option permits the user to suppress all point labeling.

3.3.2 Restricting Plotted Phase Fields

The following options control which phase fields (i.e., univariant points and curves) will be plotted by PSVDRAW. These options are useful for determining the stability fields of assemblages or individual phases. Note that PSVDRAW does not have information on the saturated-phase assemblages, and therefore it cannot be used to determine these.

```
Restrict phase fields (y/n)?
y
Suppress high-variance equilibria (y/n)?
n
```

This option is only relevant for problems in which there are solution phases stable in the thermodynamic composition space (Tut Sect 5).

```
Restrict phase fields (y/n)?
y
Show only with assemblage (y/n)?
y
Enter the name of a phase present in the fields
(left justified, <cr> to finish):
m(h&p)
Enter the name of a phase present in the fields
(left justified, <cr> to finish):
an
Enter the name of a phase present in the fields
(left justified, <cr> to finish):
```

This option permits the user to plot only those phase fields which contain **all** the phases of a specified assemblage.

```
Show only without phases (y/n)?
y
Enter the name of a phase  absent in all fields
(left justified, <cr> to finish):
cz
Enter the name of a phase  absent in all fields
(left justified, <cr> to finish):
```

This option permits the user to plot only those phase fields which **do not** contain any of the specified phases.

```
Show only with phases (y/n)?
y
Enter the name of a phase present in all fields
(left justified, <cr> to finish):
clin
Enter the name of a phase present in all fields
(left justified, <cr> to finish):
```

This option permits the user to plot only those phase fields which contain **any** one, or more, of the specified phases.

```
1 curves have the assemblage: m(h&p)     an
5 curves have one of the phases: clin
2 curves have none of the phases: cz
2 points have the assemblage: m(h&p)     an
4 points do have one of the phases: clin
```

```
1 points do not have any of the phases: cz
```

If more than one type of restriction is specified, PSVDRAW plots all phase fields which satisfy any one of the restrictions. Once PSVDRAW determines that a phase field meets the requirements of a restriction, it does not attempt to determine if the field meets the requirements of any other restrictions. Consequently, the above message only indicates the number of fields plotted because of a particular restriction, but it does not necessarily indicate the total number of fields which satisfy the restriction. For example, suppose that in the above case all the phase fields contained the assemblage m(h&p) + an, then PSVDRAW would report that no curves or points representing clin. PSVDRAW determines which fields represent assemblages first, then those that include any specified phase second, and lastly those fields that do not contain any of the specified "absent" phases. The above example does not illustrate a particularly useful application of PSVDRAW because almost all the phase fields do not contain cz, therefore PSVDRAW essentially reproduces Fig 3.3.

3.3.3 Phase Assemblage Stability Fields

The stability field of any equilibrium phase assemblage in a Schreinemakers diagram is bounded by univariant curves which connect at invariant points. However, in many geologic problems if the user asks PSVDRAW to show only phase fields containing a particular assemblage, with the goal of defining the stability field for the assemblage, PSVDRAW will not show the bounding univariant curves. This is because VERTEX identifies univariant curves by the phases with non-zero reaction coefficients in the associated reaction equation, and **not** by the complete c+1-phase equilibrium assemblage, i.e., VERTEX does not list all the phases which coexist in univariant equilibrium, but rather only those phases which are necessary to write the reaction equation. In contrast, invariant points are identified by all c+2 phases of the invariant equilibrium; therefore although PSVDRAW will not necessarily plot the bounding univariant curves of a stability field, it will always plot the bounding invariant points. As an example consider the stability field of dol + phl in Fig 3.3, this is the trapezoidal region bounded by invariant points (3), (4), (5), and (6). if PSVDRAW were asked to plot all fields with this assemblage, the only univariant curve drawn would be dol = phl + an, but all four bounding invariant points would be plotted. If a specified phase assemblage consists of fewer than c phases then, generally, some phase fields within the stability field of the assemblage will be plotted in addition to the bounding fields. Therefore, care should be taken in interpreting the stability fields defined by PSVDRAW.

3.4 Print File Output

The print file output consists of five parts: (i) a title segment; (ii) a composition diagram calculated for the thermodynamic composition space at the minimum values for both the independent potential variables of the Schreinemakers diagram; (iii) the loci and reaction equations of the stable univariant equilibria; (iv) the loci of the stable invariant equilibria; and (v) lists summarizing the univariant and invariant equilibria. The first two parts are identical to the output generated for composition diagram calculations (Tut Sect 2.12), they are reproduced here for the sake of completeness.

3.4.1 Title Segment

```
Problem title: A Schreinemakers Diagram (CaO-MgO)

Thermodynamic data base from: HOLLAND AND POWELL 1994
Fluid equation of state: Holland and Powell 1991 (CORK)

independently constrained potentials:
    X(CO2)   T(K)     P(bars)
saturated phase components:
```

```
    H2O      CO2
saturated or buffered components:
    SIO2     KALO3    AL2O3
components with unconstrained potentials:
    CAO         MGO
Phases and (projected) mol fraction MGO:
  ant      1.000  mgo      1.000  cao      0.000  cel      1.000
  ma       0.000  phl      1.000  east     1.000  clin     1.000
  ames     1.000  an       0.000  en       1.000  o-di     0.500
  mgts     1.000  di       0.500  c-en     1.000  cats     0.000
  wo       0.000  pswo     0.000  py       1.000  gr       0.000
  tr       0.714  hb       0.667  ap       1.000  cumm     1.000
  zo       0.000  cz1      0.000  cz       0.000  law      0.000
  fo       1.000  mont     0.500  crd      1.000  mctd     1.000
  mst      1.000  ta       1.000  tats     1.000  br       1.000
  chr      1.000  pre      0.000  pump     0.200  geh      0.000
  ak       0.333  merw     0.250  ty       0.000  rnk      0.000
  spu      0.000  me       0.000  cc       0.000  arag     0.000
  m(h&p)   1.000  m(t&c)   1.000  dol      0.500  sp       1.000
  vsv      0.095  mcar     1.000  lime     0.000  per      1.000
```

3.4.1.1 Phase on Saturation and Buffering Surfaces

```
phases on saturation and buffering surfaces:
  sio2      q         bq        coe       kf        san       kals
  lc        al2o3     mu        dia       pyhl      and       ky
  sill      cor
```

In comparison to the problem in Tut Sect 2, here the number of phases which may become saturated is relatively large. The possible saturated-phases are listed in the order of the saturated components they may represent, i.e., sio2, q, bq, and coe may represent the SiO_2–composant, kf, san, kals, and lc may represent the $KAlO_2$–composant, and al2o3, mus, dia, pyhl, and, ky, sill, and cor may represent the Al_2O_3 - composant. The compounds al2o3 and sio2 are fictive composants (Tut Sect 2.9), they are not necessary for this calculation but were not excluded. Should a fictive composant appear as a stable saturated phase the calculation is invalid and must be repeated with the fictive composant excluded.

3.4.2 The (Binary) Composition Diagram

```
the stable assemblages at:
                          X(CO2)   =       0.
                          T(K)     =  673.000
                          P(bars)  =  2000.00
are:
cz        clin
these assemblage(s) are compatible with the following phases or species
determined by component saturation or buffering constraints:
q         kf        mu
```

The composition phase diagram output here is for the lower-left corner of the Schreinemakers diagram (Fig 3). In this case the composition diagram is extremely simple as there is only one stable phase assemblage possible in the thermodynamic composition space (cz + clin), this assemblage coexists with pure H_2O-fluid (the saturated-phase), and the phases q + kf + mu determined from the component-saturation constraints.

3.4.3 Computational Results

The univariant phase field section is prefaced by commentary which echoes any potential variable constraints imposed for the problem (here, constant pressure), and informs the user of the coordinates to be output for each univariant field (here, the X^{f}_{CO2}–T coordinate pairs will be output for each field).

```
The X(CO2)-T(K) loci of (pseudo-) univariant fields follow:

the fields are subject to the constraint(s):

                         P(bars) = 2000.00

These fields are consistent with saturation or buffering constraints
on the component(s): SIO2   KALO3  AL2O3
```

The significance of the next two statements is clarified in the next section.

```
NOTE: For each field the values of the dependent extensities are output for
the first equilibrium condition, in general these properties vary with the
independent potentials.

Reaction equations are written such that the high T(K) assemblage is on the
right of the = sign.
```

3.4.3.1 Univariant Fields, Reactions, and Alphas and Deltas

VERTEX writes the following information for each univariant field:

```
(  1-1) cc = cz

         Alpha(-1.00, 0.500)
         Delta(  SIO2 ) =-.750     (saturated composant=q)
         Delta(  KALO3) =-.750     (saturated composant=kf)
         Delta(  AL2O3) =0.750     (saturated composant=mu)
         Delta(  H2O  ) =-.500     (saturated phase component)
         Delta(  CO2  ) =-1.00     (saturated phase component)
         Delta(-V(j/b)) =-4.76     (dependent conjugate of P(bars))
         Delta(S(j/k) ) = 152.     (dependent conjugate of T(K))

0.282527E-01  673.000      0.291267E-01  674.000      0.300277E-01  675.000
 ...
0.628314E-01  698.922      0.628470E-01  698.930      0.628547E-01  698.934

the equilibrium extends to invariant point (  1)
```

Each univariant field is identified by the thermodynamic reaction equation and a label consisting of two integer numbers in parentheses. The first integer number is the reaction index, it is used to identify the reaction in the lists at the end of the print file and it may be used to identify the univariant field in plots generated by PSVDRAW. The second number is a flag which indicates the true variance of the field, if the field is truly univariant this flag is 1. In the present example, in which there are no solution phases in the thermodynamic composition space, all the univariant fields represent true univariant equilibria. More generally, it is possible that some of the univariant fields output by VERTEX represent divariant or higher variance phase fields in which case the second integer would be 2. VERTEX uses a reaction equation of the general form:

$$0 = \sum_{i=1}^{p} \alpha_i \phi_i ,$$

where p is the number of phases in the reaction, ϕ_i is a vector containing the amounts of the thermodynamic components per mole of phase i, and α_i is the reaction coefficient of phase i. The numbers following alpha in the second line of the above output are the values of α_i's for the phases in the same order as they are output in the first line. Thus, in this case the thermodynamic reaction equation is:

$$0 = -1\, \phi_{cc} + \frac{1}{2}\, \phi_{cz} \quad \text{or} \quad 1\, \phi_{cc} = \frac{1}{2}\phi_{cz}.$$

For each reaction equation, VERTEX also computes the molar change in every dependent extensive property (i.e., any extensive property whose value is determined entirely by the independent potentials or saturation constraints. The change in a property Ψ_j, $\Delta\Psi_j$, is computed as:

$$\Delta\Psi_j = \sum_{i=1}^{p} \alpha\, \Psi_{ij}.$$

If the property Ψ_j is a saturated component, the corresponding DELTA represents the molar amount of the phase which represents that component, **not** the amount of the component itself. The identities of the phases determined by component saturation constraints, i.e., the composants, are printed with the corresponding Delta. If Φ_i is a vector which defines all n independent extensive properties of a phase, then:

$$0 = \sum_{i=1}^{p} \alpha_i\, \Phi_i - \sum_{j=1}^{n-c} \Delta\Psi_j$$

is the general reaction equation, i.e., an equation which balances all the extensive properties of the phases in the reaction; in this case the reaction may be written:

$$0 = -1\, \Phi_{cc} + \frac{1}{2}\, \Phi_{cz} + \frac{3}{4}\, \Phi_{q} + \frac{3}{4}\, \Phi_{kf} + \frac{1}{2}\, \hat{n}_{H2O} + 1\, \hat{n}_{CO2} - \frac{3}{4}\, \Phi_{mu} - 4.76\, \hat{V} - 152\, \hat{S},$$

where $\hat{n}_{H2O}$, $\hat{n}_{CO2}$, $\hat{S}$, and $\hat{V}$ are unit quantities of H_2O, CO_2, entropy, and volume. Most users are only interested in the complete chemical reaction, in this case if the relevant composition vectors are represented by the phase, or component, names the above reaction can be written:

$$\text{cc} + \frac{3}{4}\,\text{mu} = \frac{1}{2}\,\text{cz} + \frac{3}{4}\,\text{q} + \frac{3}{4}\,\text{kf} + \frac{1}{2}\,H_2O + CO_2,$$

where $\Delta S = 152$ J/K and $\Delta V = 4.76$ J/bar (47.6 cm^3).

The values for the Deltas output for each field are determined at the first $P{-}T{-}X^{f}_{CO2}$ coordinate determined for the equilibrium (i.e., the first independent variable coordinate pair output). These values may change as the loci of the phase field is traced, in particular it is important to realize that the saturated composants may change and that this may have a drastic effect on the reaction stoichiometry and properties.

The independent variable coordinates for the univariant curve, or a segment of it, are output following the reaction equation. VERTEX always traces the stability of a c+1 phase univariant equilibria, but if one or more phases in an equilibrium has a zero reaction coefficient it is possible that the same c+1 phase equilibrium will not be stable along the entire length of univariant curve identified only by the phases with non-zero coefficients (in principle such univariant curves represent several different equilibria). Thus, the conditions for what appears to be only a segment of a continuous univariant curve may be output at a given point in the print file. The same univariant curve, but usually different segments of it, may appear many times throughout the plot file. For example, consider the cc = an curve in Fig 3.2 which passes from invariant point (1), through invariant points (2) and (5) to the right-hand edge of the diagram. At invariant point (1) this curve represents the (c+1)-phase equilibrium cc + an + clin, but this equilibrium becomes metastable with respect to cc + an + phl to the right of invariant point (2), and to the right of invariant point (5) the univariant equilibrium will be cc + an + dol. Thus, the univariant curve will be output as at least three segments in the print file.

If no errors occur during the tracing of a univariant curve segment, the segment will be traced to an edge of the diagram or to an invariant point. In the latter case, as above, VERTEX prints the identity of the invariant point. Once such a point has been identified, VERTEX then traces all the univariant curves which emanate from this point and keeps track of any new invariant points. This process is repeated for sequentially for any new invariant points identified. For each invariant point VERTEX prints a message of the form:

```
equilibria about invariant point (  1):

   cz clin cc an

are listed below:
```

before enumerating the new univariant curves that emanate from the invariant point. Note that following such a message VERTEX usually only outputs curve segments that have not already been output, i.e., VERTEX generally does not output all the univariant curves emanating from an invariant point following the identification of the point.

3.4.3.2 Invariant Phase Fields

```
(Pseudo-) invariant points are summarized below:

(  1-1) cz clin cc an
               occurs at:
                         X(CO2)  =0.628547E-01
                         T(K)    = 698.934
                         P(bars) = 2000.00
 ...
```

After the loci of all the univariant curve segments have been output, VERTEX prints a list of the loci of the invariant points identified. As is the case for univariant fields, two integers are associated with each invariant field, the first number is an identifier (used by PSVDRAW) and the second indicates the true variance of the field. A value of 1 indicates the field is a true invariant field, whereas a value of 2 indicates that the field is only pseudo-invariant (Tut Sect 5).

3.4.3.3 Degenerate Invariant Phase Fields

In highly degenerate systems more than one invariant field may occur at the same P–T–X^f_{CO2} condition, VERTEX may or may not identify overlapping invariant fields depending on the reliability level specified for the calculation. For example, consider the aluminosilicate triple point in the system SiO_2–Al_2O_3, at this P-T condition either quartz or corundum may coexist with the 3 aluminosilicate phases; thus, there are 2 possible c+2 phase assemblages, q + and + sil + ky and co + and + sil + ky, at the triple point.

3.4.4 Phase Field Lists

```
(Pseudo-) invariant points are summarized below:

(  1-1) cz       clin     cc       an
(  2-1) clin     cc       an       phl
(  3-1) clin     cc       phl      dol
(  4-1) clin     dol      phl      m(h&p)
(  5-1) cc       phl      dol      an
(  6-1) dol      phl      m(h&p)   an
(  7-1) phl      an       m(h&p)   crd

(Pseudo-) univariant equilibria are summarized below:

(  1-1) cc = cz
(  2-1) cz = an
(  3-1) cc = an
(  4-1) clin = phl
(  5-1) dol = clin cc
(  6-1) dol = cc phl
(  7-1) m(h&p) = clin
(  8-1) m(h&p) = phl
(  9-1) dol = phl an
( 10-1) dol = m(h&p) an
( 11-1) phl = crd
( 12-1) m(h&p) = crd
```

The last section of the output lists all the phase fields identified by VERTEX. If the user is able to plot the output from PSVDRAW, these lists in combination with the plot are all that is needed to interpret the computational results. Thus it might be possible to secure the happiness of an innocent tree if the user restricts himself to printing the title information and these lists, rather than the entire file.

Chapter 4

AN AFM DIAGRAM: SOLUTION PHASES AND IMAGINARY COMPONENTS

The previous chapters have considered problems in which all the phases in the thermodynamic composition space are compounds; however, in many geologic systems the compositional variations of minerals have profound effects on their stability. For some time, geologists have treated such problems by computing phase relations in an endmember chemical subsystem where no compositional variations are possible. Activity corrections are then made to account for difference between the observed mineral compositions and their compositions in the endmember subsystem. In effect, in this approach solutions are treated as compounds in a simpler composition space, thus it is a misnomer to claim that such methods treat phases of variable composition. Activity corrections can be made with the program Actcor which generates a new thermodynamic data file that can be used as an input file for BUILD and VERTEX. However, the activity correction method is fundamentally flawed in two ways: (i) the compositions of the minerals in an equilibrium phase assemblage will vary as a function of the systems variables, but this possibility is precluded in fixed-activity calculations; and (ii) the compositions for the activity corrections are assumed to be equilibrium compositions and no tests are made to validate this assumption, which is generally not consistent with the thermodynamic models being used. For these reasons, activity corrections should only be used as a method of last recourse.

The alternative to the activity corrections, is to make calculations in the full composition space, or a reasonable approximation. The compositions of the minerals are then variables which are determined for every composition and environmental condition. For such calculations to be feasible there must be thermodynamic data for every possible endmember composition of every possible solution phase in the system, and it must be possible to formulate at least a rudimentary model of how these endmembers mix.

4.1 The Pseudocompound Approximation

In VERTEX variable composition phases are approximated by a series of arbitrarily defined compounds designated pseudocompounds. By this method VERTEX can treat solutions with up to 3 independent mixing sites and up to 3 species mixing on each site. The accuracy of the approximation depends on how closely spaced the pseudocompounds are in composition space, this is determined by the subdivision scheme specified by the user in a file that describes the solution models for VERTEX (the version of this file supplied with PeRpLeX is named `solut.dat`). The details of how to formulate solution models for PeRpLeX are described in depth, with examples, in Doc Sect 1.3, 1.4 & 4 and are not treated further here. Although formulation of new models may be too complicated for some users to undertake, modification of subdivision schemes used for existing models is relatively straight forward (Doc Sect 1.4 & 4). Examples of these subdivision schemes are illustrated in Fig 4.1; by varying the parameters for these schemes it is possible to obtain almost any degree of accuracy.

4.2 Imaginary Components

In the classical AFM projection, compositions are reduced by successive projections through H_2O, SiO_2 (quartz), KAl_3O_5 (muscovite) onto the subcomposition MgO-FgO-Al_2O_3. This projection can be made with VERTEX as discussed in Tut Sect 3.1, by specifying water as a saturated phase and SiO_2 and KAl_3O_5 as saturated components (the latter being defined by a component transformation from K_2O). The difficulty with this projection is that after it is done phlogopite (phl, $KMg_3AlSi_3O_{12}(OH)_2$ => Mg_3Al_{-2}) and annite (ann, $KFe_3AlSi_3O_{12}(OH)_2$ => Fe_3Al_{-2}) have negative compositions in the MgO-FgO-Al_2O_3 subcomposition, i.e., they plot outside the MgO-FgO-Al_2O_3 ternary. Phases with negative compositions are automatically excluded by VERTEX, so it is necessary to introduce a component transformation to make the compositions positive. While it may seem paradoxical, this can be done by replacing the "real" components MgO and FeO by the "imaginary" components M (Mg_3Al_{-2}) and F (Fe_3Al_{-2}) so that the compositions of ann and phl become "real," i.e., positive. Of course it is not necessary that you define the imaginary components to correspond to real phases, but unless you do it will also be necessary create an imaginary composant in the thermodynamic data file for each imaginary component (Tut Sect 2.9, Doc Sect 1.6).

4.3 Running BUILD

No new prompts appear from BUILD for this calculation, as compared to that in Tut Sect 2, and only the component transformations, component choices and solution model prompts are shown here. The thermodynamic data file used for this example was `hp94ver.dat.`

4.3.1 Component Transformations

For this problem the user must make three component transformations as in Tut Sect 3.2.2: (i) replacing component K_2O by the component K (KAl_3O_5) = 0.5 K_2O + 1.5 Al_2O_3, this component is the muscovite endmember composition after projection through water and quartz. (ii) replacing component FeO by the component F (Fe_3Al_{-2}) = 3 FeO – Al_2O_3, this component is the annite endmember composition after projection through water, quartz, and muscovite. (iii) replacing component MgO by the component M (Mg_3Al_{-2}) = 3 MgO – Al_2O_3, this component is the phlogopite endmember composition after projection through water, quartz, and muscovite. Note that by defining component K to permit projection through stoichiometric muscovite, K-feldpars will have negative compositions and be rejected by VERTEX. Consequently, VERTEX will not recognize any thermal limit for muscovite stability and the calculations will only be valid within the stability field for muscovite + quartz (Tut Sect 3.1)

The user then specifies water fluid as a saturated phase (Tut Sect 2.4), two saturated components with the saturation hierarchy SiO_2-KAl_3O_5 (Tut Sect 3.1), and Mg_3Al_{-2}, Fe_3Al_{-2} and Al_2O_3 as thermodynamic components.

4.3.2 Solution Model Prompt

PeRpLex is supplied with a file named `solut.dat` containing a number of different models for phases of geologic interest. Some of these models (particularly for non-ideal solutions) may have limited ranges of applicability, and before you seriously use any results from PeRpLeX you should carefully check the models you are using.

```
Enter the solution model file name (e.g. solut.dat),left justified:
solut.dat
```

Following this prompt VERTEX checks each model in the file to determine if it is appropriate for the selected components and endmembers. A model may be inappropriate because all its endmembers either do not lie within the composition space for the problem, do not exist in the thermodynamic data file, or have been excluded by the user. In these cases BUILD issues a warning such as:

```
**warning ver025** no endmembers for humite, the solution will not be
considered.
```

If some, but not all, the endmembers are identified BUILD will attempt to recast the model as a simpler solution, for example the ternary grossular-pyrope-almandine model GrPyAl(B) can be used as a model for pyrope-almandine garnet. Because the rules BUILD use for recasting may not produce the results (particularly the subdivision scheme) the user wants, BUILD issues the warning:

```
**warning ver117** the subdivision scheme for GrPyAl(B) will be interpreted
as a binary model on site 1 (originally site 1) with:
           imod= 0
           xmax=   1.000
           xmin=   0.000
           xinc=   0.100
To change this, or if an error (probably from routine CART) follows,
modify the solution model (documentation sect. 4.1)
```

For single site models such as GrPyAl(B), recasting is usually successful because there are relatively few choices involved. However for multi-site models care should be taken to avoid unpleasant surprises. If BUILD cannot recast a multi-site model, or if only one endmember for a solution model is found, it issues the warning:

```
**warning ver034** Neph(F&B)  could not be recast as a simpler model.
The solution will not be considered.
```

Once BUILD has identified valid solution models it writes the prompt:

```
Select phases from the following list, enter the
names one at a time and left justified, ENTER A BLANK WHEN YOU ARE DONE.

 Chl         Tlc         Bio         K-Phen      St          Carp
 Crd         Cumm        Anth        EnFs        Ol          Sp(J&R)
 Sp(G&S)     Sp(G)       Sp          Gt(i-b)     Gt(i-c)     Ctd
 Gt(isa)     GtD         Gt          GrPyAl(B)
```

In response to this prompt the user selects the models: **`Chl, Crd, Bio, St, Gt`** and **`Sp`**

Some solution model names may be cryptic and the user has no choice but to read the comments (or endmember identities) in the solution model file to determine what phase they represent. Several models for the same solution may be available (e.g., here there are five garnet models Gt(isa), GtD, Gt, GrPyAl(B), Gt(i-c)). In some cases it may be desirable to use two or more models to describe a single solution, for example to minimize computations it is possible to use a model that provides very coarse resolution of compositions that are unimportant, and a second high resolution model in the region of interest. Often it is also useful to use two models for a solution that may exhibit immiscibility.

4.3.3 Solution Models for the Saturated (Fluid) Phase

As currently set up, the only possible saturated phases are molecular fluids. There are also "solution" models (actually they are only subdivision schemes) for molecular fluids (e.g., models Fluid, F, and H2OM in the solut.dat); however, if you specify fluid as a saturated phase then do not choose these models as solutions. Usually BUILD will not allow you to this, hence the warnings:

```
**warning ver113** Fluid is not a valid model because component H2O or CO2 is
```

```
constrained.

**warning ver025** no endmembers for F the solution will not be considered.

**warning ver025** no endmembers for H2OM the solution will not be considered.
```

These models are only applicable if the components of the fluid are specified as thermodynamic components; as is necessary for the construction of petrogenetic grids for all possible fluid compositions and fluid-absent conditions (Connolly & Trommsdorff 1991, Connolly 1994).

4.3.4 Projection Through Solution Phases

It is often said, following Greenwood (1975), that it is only possible to project through the composition of phases with fixed compositions. This is not true, and through specification of a component saturation in VERTEX it is possible to project through solution phases. Provided this is done correctly VERTEX will establish the stable composition of the solution as a function of the independent potential variables and other saturation constraints. The last prompt (4.3.2) lists K-Phen (phengitic muscovite) as a possible solution. Because the calculation is for a system saturated in muscovite component, selecting K-Phen would require extension of the thermodynamic composition space to include celadonites (after projection through SiO_2 and KAl_3O_5), i.e., definition of components M and F as $MgAl_{-2}O_{-2}$ and $FeAl_{-2}O_{-2}$, respectively. However this would have catastrophic consequences, because VERTEX would always identify the two most muscovite-rich phengite pseudocompounds as being the stable phases at the M and F apices of the diagram. In other words, the composition of the K-Phengite phase would be determined by muscovite component saturation, and not by the real equilibrium phase relations. An example of a valid solution phase projection would be the projection of ilmenite-hematite solution in a rutile saturated system as an implicit or explicit function of μ_O or X_O.

As a general rule, **it is never possible to consider a solution phase that lies entirely or partially within the saturated component composition space if an endmember of the solution is stable in this composition space.** In this example, ignoring the phengite component in muscovite is a reasonable approximation, provided the muscovite phengite content is not specifically of interest (if it is why use the AFM?). The effect of this approximation is to raise μ_{KAl3O5}, resulting in a slightly larger stability for potassic phases (biotite). Whether this effect is significant or not can be tested by doing a calculation without projection through muscovite, i.e., by adding $KAlO_3$, K_2O, or KAl_3O_5 as a thermodynamic component and including K-phengite as a solution. If the compositions of the AFM minerals coexisting with K-Phengite in this extended calculation differ significantly from the AFM calculation as done here, then clearly the effect of phengite solution can not be ignored.

4.4 Composition Diagram Output for Problems with Solutions

Running VERTEX and PSVDRAW for a problem with solution models is no different than in the examples illustrated earlier.

4.4.1 Pseudocompound Names

All output from VERTEX for composition diagram calculations is done in terms of pseudocompounds. Pseudocompounds are named in terms of the solution endmembers and not the solution name itself. Thus the user must determine from the solution model, or pseudocompound stoichiometry, which endmembers belong to which solution. In the present example the pseudocompounds correspond to solutions as indicated below:

```
phases and (projected) composition with respect to F     and AL2O3 :
```

```
ant       0.00  0.50        al2o3     0.00  1.00        mgo       0.00  0.50
 ...
```

Pseudocompounds for Chl (chlorite) a solution among clin (clinochlore), da (daphnite), ame (amesite) and fame (ferroamesite):

```
 ...
cl12-16   0.26  0.70        cl14-16   0.26  0.70        cl17-16   0.25  0.70
 ...
```

Pseudocompounds for Bio (biotite) a solution among phl (phlogopite), ann (annite), east (eastonite) and sdph (siderophyllite):

```
 ...
ph19-80   0.70  0.13        ph29-80   0.61  0.13        ph39-80   0.53  0.13
 ...
```

Pseudocompounds for St (staurolite) a solution between mst (magnesiostaurolite), and fst (ferrostaurolite):

```
 ...
ms2.5     0.11  0.89        ms5       0.11  0.89        ms7       0.11  0.89
 ...
```

Pseudocompounds for Crd (cordierite) a solution between crd (cordierite), and fcrd (ferrocordierite):

```
 ...
cr16      0.17  0.80        cr24      0.15  0.80        cr33      0.13  0.80
 ...
```

Pseudocompounds for Ctd (chloritoid) a solution between mctd (magnesiochloritoid), and fctd (ferrochloritoid):

```
 ...
mc50      0.10  0.80        mc58      0.08  0.80        mc66      0.07  0.80
 ...
```

Pseudocompounds for Gt (garnet) a solution between py (pyrope), and alm (almandine):

```
 ...
py9       0.30  0.67        py18      0.27  0.67        py27      0.24  0.67
 ...
```

The conventions used for naming pseudocompounds are listed below:

4.4.1.1 Binary Single Site Solutions

Pseudocompound names are the first two letters of the first endmember of the solution followed by its percent mole fraction, e.g., ms2.5 is a staurolite pseudocompound composed of 2.5 mole % mst and 97.5 mole % fst. If two solutions have endmembers that begin with the same letters, the resulting names are ambiguous. This problem can be avoided by switching the positions of the endmembers in one of the model definitions.

4.4.1.2 Ternary Single Site Solutions

Pseudocompound names are the first letter of the first two endmembers followed by the mole fraction of the endmember, e.g., for solution ABC the pseudocompound A10B20 is composed of 10 mole % endmember A, 20 mole % endmember B and 70 mole % endmember C.

4.4.1.3 Two Binary Site Solutions

Pseudocompound names are the first two letters of the first endmember followed by the mole fractions of that endmembers site species on the first and second sites, separated by a hyphen. To decipher these names it is necessary to determine from the solution model (or pseudocompound compositions) which species mix on which site. Taking Chl (chlorite) as an example, M1 is the first independent site and Mg and Fe mix on this site, and T2 is the second independent mixing site and SiAl and Al_2 mix on this site (see file solut.dat and Doc Sect 1.3.1 for elaboration). Clinochlore endmember has Mg on M1 and SiAl on T2, thus the pseudocompound cl14-16 has $X_{Mg}^{M4} = 0.14$ and $X_{SiAl}^{T2} = 0.16$, or the composition $(Fe_{3.44}Mg_{0.56})^{M4}(Fe_{0.13}Mg_{0.02}Al_{1.85})^{M2}(Si_{0.16}Al_{1.84})^{T2}O_{10}(OH)_8$, where the M2 site population is determined by the M1 and T2 populations.

4.4.1.4 Other Multiple Site Solutions

Pseudocompound names are given by the site fractions of the first c-1 species on each site sequentially in units of 10 mole %. For a three site model $(ABC)^{I}(DE)^{II}(EF)^{II}$, the designation 5346 indicates 50 % A and 30 % B on site I, 40% D on site II, and 60 % E on site III. For such compounds VERTEX also outputs a special list giving the mole fraction of each endmember.

4.4.2 Pseudocompound Assemblages

As a result of the pseudocompound approximation all the assemblages consist of as many compounds as there are thermodynamic components. In this example each assemblage therefore consists of three phases (in addition to the saturated phases), the abridged listing of these assemblages follows:

```
the stable assemblages at:
                          P(bars)  =  4000.00
                          T(K)     =  840.000
                          Y(CO2)   =       0.
are:
 ...
and     -cl83-50 -cl75-50 (2)       ms2.5   -py9     -cl24-50 (1)
and     -ms5     -cl41-50 (1)       ms2.5   -ms5     -cl24-50 (2)
ph83-89 -ph91-80 -ph83-80 (3)       ph75-89 -ph83-80 -ph75-80 (3)
ph66-89 -ph75-80 -ph66-80 (3)       ph58-89 -ph66-80 -ph58-80 (3)
ph50-89 -ph58-80 -cl50-62 (2)       ph41-89 -cl50-62 -cl41-62 (2)
ph33-89 -cl41-62 -cl33-62 (2)       ph24-89 -cl33-62 -cl24-62 (2)
 ...
these assemblages are compatible with the following phases or species
determined by component saturation or buffering constraints:
q         mu

** no immiscibility occurs in the stable solution phases **
```

4.4.2.1 Variance of Pseudocompound Assemblages

Although each pseudocompound assemblage consists of three compounds or pseudocompounds, a given assemblage will correspond either to a three-phase region, a part of a two-phase region, or a part of a one phase region in the true AFM diagram. VERTEX distinguishes these cases as indicated by the integer in parentheses following each assemblage:

(0) The assemblage consists entirely of true compounds.

(1) The assemblage is invariant, i.e., every pseudocompound represents a different solution. For example, the andalusite + staurolite + chlorite AFM assemblage {and-ms5-cl41-50 (1)}.

(2) The assemblage is part of a high variance heterogeneous phase region. For example, the pseudocompound assemblage {ph33-89-cl41-62-cl33-62 (2)} comprises part of the biotite + chlorite AFM assemblage. The averaged compositions of the pseudocompounds in such assemblages can be used to estimate the compositions of coexisting phases, the assemblage {ph33-89+cl41-62+cl33-62 (2)} suggests $X_{Mg}^{Chl} \approx 0.37$ and $X_{Mg}^{Bio} \approx 0.33$ in the coexisting phases.

(3) The assemblage is part of a homogeneous phase region. For example, the assemblage {ph83-89+ph91-80+ph83-80 (3)} is part of the biotite phase region.

(4) The assemblage contains includes two or more phases of an immiscible solution. VERTEX tests for immiscibility by determining whether the compositions of pseudocompounds from a solution in an assemblage span the composition of an additional compound of that solution.

4.4.3 Plotted Output

Fig 4.2 shows the plot generated by PSVDRAW. PSVDRAW only writes the names of pseudocompound assemblages that correspond to invariant compositions. Invariant 3-phase regions are drawn with heavy solid lines. Pseudocompounds in divariant 2-phase regions are connected by short dashed lines that approximate tielines. One-phase regions are shaded. Pseudocompounds within solvi are connected by long dashed lines approximating tielines. These plotting rules may lead to several peculiarities illustrated in Fig 4.2: (i) The stable compositions of binary solutions are shown only by dashed lines, e.g., Gt and Chl are stable between py18 and alm and cl83-62 and cl58-62, respectively. (ii) If a two phase region, such as Bio + ky, is the same width as the pseudocompound spacing, no dashed "tielines" will be visible within it. (iii) Every tieline is drawn twice, in some cases this overlapping causes dashed lines to appear as solid lines (e.g., the thin solid lines within the Chl + Bio and Gt + Bio fields. It may also be noted that although Chl is a ternary solution due to variable Mg:Fe ratio and Tschermaks substitution, it appears as a binary Mg-Fe solution in Fig 4.1. This is an artifact of the pseudocompound approximation and indicates that the maximum range in Tschermaks content is less than the assigned spacing between pseudocompounds for this substitution (a spacing of about 12% of the possible range was used for the calculation).

Chapter 5

MIXED-VARIABLE AND SCHREINEMAKERS DIAGRAMS WITH SOLUTION PHASES

A Mixed-Variable diagram is any diagram in which compositional variables of the system are plotted against a potential variable or related quantity (P, T, μ_i, X^f_{CO2}, X^f_O, f_i, or a_i, etc.), the most common petrological examples of mixed-variable diagrams are the T-X eutectic diagrams used in igneous petrology. PSVDRAW can only plot two-dimensional diagrams, so to obtain plotted mixed-variable diagrams with PeRpLeX it is necessary to limit calculations to systems with two thermodynamic components. The invariant reactions of mixed-variable diagrams correspond to the univariant reactions of Schreinemakers projections. For this reason, it is often useful to calculate multi-dimensional mixed-variable diagrams as an aid in interpreting complex Schreinemakers projections, or to verify the integrity of a projection computed by VERTEX.

Computational problems with solution phases involve only a few prompts from BUILD or VERTEX that have not been discussed in earlier Chapters. Accordingly, this Chapter focuses on the output generated by VERTEX and PSVDRAW.

5.1 Running BUILD for a Mixed-Variable Diagram

The system K_2O-MgO-FeO-Al_2O_3-SiO_2-H_2O will be considered here. To reduce the problem to one with two thermodynamic components, water will be treated as a saturated phase, and the component saturation hierarchy SiO_2-Al_2O_3-K_2O will be applied. At the conditions of interest the component saturation hierarchy implies that all phase assemblages in the thermodynamic composition space (MgO-FeO) will coexist with quartz, aluminosilicate, and muscovite or K-feldspar. This projection is equivalent to looking at the phases that coexist with the aluminosilicate at the A-apex of the AFM diagram (Tut Sect 3) as a function of X_{Mg} For the example here, `hp94ver.dat` and `solut.dat` were used as the thermodynamic and solution model files. Both print and plot files were requested, the print file format prompt is irrelevant. No phases were excluded from the calculation, and the solutions models `Gt, Bio, Gt, Chl, Ctd, Crd` and `Sp` were included. The calculation was made at P = 7 kbar, for T = 803-913 K.

5.1.1 Reaction Equation Format Prompt

For mixed-variable diagrams, by default, VERTEX will only output an abbreviated reaction equation including only those phases that are within the thermodynamic composition space. Additional information, such as the stoichiometric coefficients, stable phases in the saturated component space, or the entropy and volume change of the reaction, can only be obtained by requesting extended reaction equation format (Tut Sect 3.2.2).

5.2 Mixed-Variable Diagram Output

The print file output by VERTEX for mixed-variable diagram consists of a title segment (as for earlier examples), followed by a list of reactions and their equilibrium conditions. The abridged listing below begins with the binary composition diagram output in the title segment:

```
 ...
the stable assemblages at:
                          T(K)     =  803.000
                          P(bars)  =  7000.00
                          Y(CO2)   =       0.
are:
fctd      mc8       mc16      cl50-50   cl57-50   cl64-50
cl71-50   cl78-50   cl85-50   cl92-50   cl99-50
these assemblage(s) are compatible with the following phases or species
determined by component saturation or buffering constraints:
q         ky        mu

** no immiscibility occurs in the stable solution phases **
```

The stable phases are listed in the order that they occur along the FeO-MgO binary.

The title segment is followed by a list of invariant (peritectoid, eutectoid, or singular) and pseudoinvariant (explained below) equilibria. The equilibrium reactions are listed in order of increasing temperature (or more generally the independent potential). Each equilibrium is assigned a two part numerical identifier, the first number identifies the equilibrium, and the second number indicates if the reaction is invariant (1) or pseudoinvariant (2).

```
 ...
The equilibrium of the pseudoinvariant reaction:
 (   1-2) Ctd(fctd) Ctd(mc8) = St(ms2.5)
occurs at T(K)    = 815.581     and P(bars) = 7000.00
      ----------------------------------------
The equilibrium of the invariant reaction:
 (  11-1) Ctd(fctd) = St(fst)
occurs at T(K)    = 816.387     and P(bars) = 7000.00
      ----------------------------------------
The equilibrium of the pseudoinvariant reaction:
 (  10-2) Chl(cl99-50) = Chl(cl99-62)
occurs at T(K)    = 821.264     and P(bars) = 7000.00
      ----------------------------------------
 ...
      ----------------------------------------
The equilibrium of the pseudoinvariant reaction:
 (  12-2) St(ms2.5) Ctd(mc8) = St(ms5)
occurs at T(K)    = 825.390     and P(bars) = 7000.00
      ----------------------------------------
 ...
      ----------------------------------------
The equilibrium of the pseudoinvariant reaction:
 (   2-2) Ctd(mc8) = Ctd(mc16) St(ms5)
occurs at T(K)    = 826.828     and P(bars) = 7000.00
      ----------------------------------------
 ...
      ----------------------------------------
The equilibrium of the invariant reaction:
 (  16-1) Ctd(mc16) = St(ms7) Chl(cl42-62)
```

```
occurs at T(K)    = 833.272     and P(bars) = 7000.00
      ----------------------------------------
```

5.3 Pseudocompound Reactions

The default plot generated by PSVDRAW for this example is shown in Fig 5.1 (phase fields labeling within the diagram has been added). As a result of the pseudocompound approximation, VERTEX distinguishes two of reactions, invariant reactions in which every compound represents a distinct phase, and pseudoinvariant reactions in which at least two pseudocompounds represent the same phase. Invariant reactions define eutectoids or peritectoids (an upside down eutectoid) in mixed-variable diagrams (case 3, Fig 5.2). For example, Equilibrium (16) in the above listing, defines the peritectoidal decomposition of chloritoid to staurolite + chlorite. Most commonly, pseudoinvariant reactions represent the stepwise variation in phase fields that can be seen in Fig 5.1 (case 1, Fig 5.2). Pseudounivariant equilibria (12) and (2) are examples of this, such equilibria can be thought of as defining an isopleth at which the true composition of the solution is given by the average of the pseudocompound compositions.

It is also possible that a pseudoinvariant reaction defines the conditions of an invariant singular reaction (case 2, Fig 5.2). Equilibria (1) above is identified by VERTEX as such a reaction; however often, and specifically in this case, such reactions are an artifact of the pseudocompound approximation. This artifact occurs frequently at the compositional extremes for solutions. It arises in this case because the staurolite compounds have a much finer compositional spacing (2.5 mol % Mg) than chloritoid (8 mol % Mg). Frequently this kind of problem can be avoided by changing subdivision schemes so that all the solutions are modeled by pseudocompounds with roughly the same compositional spacing. However it is also important to avoid using models with identical spacing because then VERTEX and PSVDRAW are unable to determine the true variance of pseudocompound reactions (Doc Sect 1.4). Another problem that arises due to pseudocompound spacing occurs when coexisting solutions have nearly the same (i.e., on the same scale as the pseudocompound spacing) compositions. For example, suppose Fe-Mg olivine (white pseudocompounds in Fig 5.3) slightly more magnesian than coexisting Fe-Mg enstatite (black pseudocompounds), and that both phases become more Fe-rich with temperature. If the pseudocompound spacing is as shown in Fig 5.3b, VERTEX and PSVDRAW will become "confused" about the kinds of reactions that occur because the approximated phase fields of olivine and enstatite interfinger. This problem would not occur with the pseudocompounds as shown in Fig 5.3a.

Two additional types of reaction occur in which all the pseudocompounds of the reaction represent a single solution phase: (i) If the solution has a solvus, such reactions define either a pseudounivariant contour of the solvus (a reaction of the form $A_1+A_9=A_2$ analogous to case 1, Fig 5.2) or the solvus critical point (a reaction of the form $A_4+A_6=A_6$). (ii) If the compositional variation of the solution is determined partially by component or phase saturation constraints, this variation will occur solely as a function of the potential variables and will involve only the solution in question. For example, the Tschermaks content of chlorite is determined by the saturation hierarchy in the above problem. Thus, as temperature is increased, the Chl pseudocompound for a given X_{Mg} must eventually change to account for changing Tschermaks activity, equilibrium (10), above, is an example of this. VERTEX does not attempt to distinguish these types of reactions, but PSVDRAW does. The conditions for equilibria of the latter type are shown by open circles (e.g., the open circles in Fig 5.1), whereas the latter are drawn as the normal stepped phase boundaries.

PSVDRAW does not label the phase fields within mixed-variable diagrams (the labeling in Fig 5.1 has been added), but by default it writes the identity of all invariant equilibria along the right border of the diagram. This information is enough to identify the diagrams phase, but to resolve ambiguity the initial phase fields can also be determined from the composition diagram given in the title segment of the print output. PSVDRAW may be very sensitive to minor flaws resulting from the pseudocompound approximation, usually these errors are obvious, but they can be subtle. Accordingly, phase relations should be carefully checked to verify that they make sense. A good test for this is to recalculate the mixed-variable diagram over a smaller interval for the independent potential and to compare this diagram to the first. In general, the smaller the interval then the lower the chance of an error.

5.4 Schreinemakers Diagrams with Pseudocompounds

Fig 5.4a shows of a Schreinemakers diagram for the system CaO-FeO-Al_2O_3-SiO_2-H_2O-CO_2-O_2. as a function of temperature and fluid composition at constant pressure (2 kbar) and μ_{O2} (-195 kJ). This system is relevant for interpreting skarn formation, but it is to be emphasized that the diagram is used mainly for purposes of demonstration, as the μ_{O2} constraint has no quantitative meaning (can you imagine a system in which μ_{O2} is independent of temperature?). To further simplify the example the system was assumed to be saturated with respect to quartz and the stable SiO_2 - CaO compound that coexists with quartz (either calcite or wollastonite, depending on T- X^f_{CO2} conditions). Two binary solutions were considered, epidote-zoisite (EpCz) and andradite-grossularite (GrAd).

As in mixed-variable diagrams it is possible to distinguish to types of equilibria. Dashed curves correspond to the equilibrium loci of a pseudounivariant assemblage, in which two or more compounds represent the same solution. These curves contour homogeneous equilibria, e.g. the pseudounivariant curve cz50 = an + cz41 can be thought of as representing the continuous decomposition of epidote by a discrete step in which the epidote becomes depleted in zoisite component with increasing X^f_{CO2}. The loci actually defines conditions where anorthite is in equilibrium with both epidote pseudocompounds, and is best interpreted as indicating conditions where anorthite is in equilibrium with an epidote composition equal to the average of the pseudocompounds (i.e. about cz45); more zoisite-rich compositions being confined to water-rich conditions. Solid lines define conditions of true univariant equilibria; ordinarily the stoichiometry of a univariant reaction involving a solution varies continuously as the composition of the solution changes; but as a consequence of the pseudocompound approximation this variation occurs discretely at pseudoinvariant points (small dots in Fig 5.4a) where one or more pseudounivariant curves intersect the univariant curve. Thus, epidote stability is limited in CO_2-rich fluids by the univariant reaction epidote = hematite (hm) + anorthite, where the epidote becomes progressively less aluminous with increasing T.

Because it is possible to show continuous equilibria in Schreinemakers projections, as well as the univariant equilibria conventionally shown, there are two ways in which the projections can be used. If only true univariant equilibrium are shown, the diagrams define the maximum stability of the possible phase assemblages of a system. For example, the assemblage anorthite + epidote is only stable within the T- X^f_{CO2} region bound by the univariant curves epidote = an + garnet (high T) and epidote = an + hm (high X^f_{CO2}). Alternatively, if the specific composition of the epidote solution is considered, then the pseudounivariant curves can be used to define a much narrower region for stability of the assemblage. This is basically a form of thermobarometry; it differs from the conventional approach in that one uses thermodynamic models to predict mineral compositions as a function of environmental variables.

Fig 5.4a is simplified in that only pseudounivariant equilibria involving one solution are shown, thus the pseudounivariant curves that show the compositions of coexisting epidote and garnet (between the epidote-out reaction epidote = an + garnet and the garnet-out reaction garnet = epidote + epidote) are not shown.

5.4.1 High Variance Phase Field Prompt

```
Calculate high variance phase fields (Y/N)?
```

The only new prompt is written by BUILD for a Schreinemakers projections follows the solution model prompts and concerns high variance phase fields. If the user answers no, the pseudounivariant equilibria will not be calculated. Calculations are slightly more reliable if these equilibria are calculated, and they can always be suppressed later in PSVDRAW.

5.4.2 PSVDRAW with Solutions

Solutions can be identified by either the name of a specific pseudocompound (e.g. cz54), or by the name of the entire solution (EpCz). The former is useful when the user is concerned with determining conditions where a specific composition of a solution is in equilibrium, whereas the latter is useful when the user wishes to determined the entire stability field for the solution in question.

Chapter 6

PHASE DIAGRAMS FOR GRAPHITIC ROCKS AND C-O-H-S FLUIDS

PeRpLeX includes a number of fluid equations of state for multispecies molecular fluids and specifically for graphitic rocks. This chapter briefly outlines some of the ways you can use these equations in VERTEX. A C-O-H fluid in equilibrium with graphite has one compositional degree of freedom (for you nitpickers, here I am disregarding the degree of freedom that would arise if fluid pressure were independent of total pressure, see Skippen & Marshall 1992). This single degree of freedom may be specified by any property of the fluid and in this regard there are two practical choices for geologic problems: (i) species potentials (i.e., the concentration, fugacity or activity of a fluid species); or (ii) a bulk compositional variable:

$$X_O^f \equiv \frac{n_O}{n_O + n_H}$$

related to the H/O ratio of the fluid (Connolly & Cesare 1993, Connolly 1994). Although species potentials are widely (ab-)used, they are actually only useful if the species is buffered by mineral equilibria at all P-T conditions of interest. In this case the fluids composition is a function only of pressure and temperature, and there is no need to consider the fluid composition explicitly (for phase diagrams). For any other situation X_O^f is the only wise choice, if you want to read more about this point I have discussed it ad nauseum in a paper in Contributions to Mineralogy and Petrology (Connolly 1994, also Connolly & Cesare 1993). The significance of X_O^f is illustrated in Fig 6.1, which shows that X_O^f varies from 0 to 1 as fluid composition varies from the C-H join to the C-O join. A fluid that is produced by the reaction of water (e.g., released by dehydration) with graphite will have X_O = 1/3, which is the C-O-H fluid composition at which the activity of water is a maximum. Another way of thinking about X_O^f is to consider a thermodynamic projection of C-O-H fluid composition through carbon. After projection the fluid becomes a binary fluid in the H-O system, and in this sense can be treated in exactly the same way we treat other binary fluids, e.g., H_2O-CO_2 mixtures. In the geologically applicable limit that a C-O-H fluid can be regarded as binary H_2O-CO_2 and H_2O-CH_4 mixtures (Connolly 1994):

$$X_{CO_2}^f \approx \frac{3\,X_O^f - 1}{X_O^f + 1} \qquad X_O^f > \frac{1}{3}$$

$$X_{CH_4}^f \approx \frac{1 - 3\,X_O^f}{X_O^f + 1} \qquad X_O^f < \frac{1}{3}.$$

The PeRpLeX program COHSRK can be use to obtain the exact speciation of the fluid at any P-T-X_O condition of interest.

Regardless of whether the user chooses to use a species potential or X_O^f as a fluid "compositional" variable, there are two methods of doing the desired calculations. In the simpler method, at least in a mechanical sense, the user tricks VERTEX into computing the three fugacities of interest (f_{O2}, f_{CO2} and f_{H2O}) as a function of a single variable without specifically referring to a carbon component. A more complex, but also more elegant, method is to actually redefine the default components for VERTEX so that the fluid composition space can be projected through the carbon component. After this projection the fluid is completely described by two components, H and O, and the resulting calculations can be interpreted in exactly the same way as those for binary H_2O-CO_2 fluids. These methods are referred to as Methods I and II, below. Method II is only strictly necessary if the user is interested in doing calculations in which the system may become fluid-absent (i.e., as in calculation of a P-T projection for all possible fluid compositions, in such cases the fluid components are treated as thermodynamic components, Tut Sect 7).

6.1 Buffered f_{O2} or f_{CO2}: Method I

In graphite-saturated systems, if a mineral equilibrium buffers the potential of any C-O-H fluid species, then fluid composition is uniquely determined as a function of P-T conditions. In principle it is possible to solve C-O-H fluid speciation as function of any species; however, it is arithmetically cumbersome to do so for H_2O. Consequently, in PeRpLeX the only fluid speciation routines currently provided are for buffered f_{O2}, which is also equivalent to buffering of f_{CO2}. This equivalence follows from the relation:

$$\mu_{CO2} = \mu_{O2} + \mu_{C},$$

where $\mu_C = \overline{G}_{graphite}$. Thus an equilibrium such as:

calcite + quartz = wollastonite + CO_2

can also be written as:

calcite + quartz = wollastonite + graphite + O_2

6.1.1 Fluid Components

If you wish do make calculations for buffered species fugacities you should answer the saturated phase prompts as follows:

```
Calculations with a saturated phase (Y/N)?
The phase is:   FLUID
Its components can be: H2O   CO2
Its compositional variable is: Y(CO2)
y
Enter number of components in the   FLUID
(1 or 2 for COH buffered fluids):
2
```

The number of components entered in response to the last prompt does not effect the way VERTEX does fluid speciation calculations, it merely defines the chemical system of interest to the user. If the user answers 2, as above, then both hydrates and carbonates are considered, whereas if the user responds with a 1, then she/he/it is asked to select either H_2O or CO_2. In this case only minerals containing the specified component will be considered.

The "trick" in method I computations comes in getting VERTEX to make use of f_{O2} of the fluid phase. For any fluid routine that uses or computes an f_{O2} for the fluid phase, VERTEX automatically looks to see if O_2 is specified as saturated component; if it is, VERTEX adds {RT ln (f_{O2})} to the reference state free energy of the O_2 component and redox equilibria consistent with the saturation constraint are computed. Thus in response to the saturated component prompt:

```
Select saturated components from the set:
NA2O  MGO   AL2O3 SIO2  K2O   CAO   TIO2  MNO   FEO   O2
How many saturated components (<8)?
1
Enter component names, left justified, one per line:
O2
```

The user must select O_2 as a saturated component if redox equilibria are to be computed. If additional saturated components are specified, it does not matter where O_2 is placed in the component saturation hierarchy. As with H_2O and CO_2, choosing O_2 as a saturated component has no effect on the fluid speciation calculations, so it is pointless to specify O_2 as a saturated component if no redox equilibria are possible in the system of interest.

6.1.2 Fluid Equations of State for Buffered C-O-H Fluids

The fluid routines that currently support C-O-H fluid buffering are choices 7 and 8. My personal bias is that routine 8 is preferable at all conditions where it converges. When these routines are selected, the user receives the following prompts:

```
Modify default buffer (max H2O) (Y/N)?
y
```

The default buffer "max H2O" is an f_{O2} buffer that corresponds to the conditions at which C-O-H fluids have the maximum thermodynamic activity of H_2O. As discussed by Connolly & Cesare (1993), this is the composition of fluids produced by entirely by dehydration in the presence of graphite, it is also the composition which dehydration reactions will buffer toward if there are no other simultaneous devolatilization processes. The "max H2O" conditions are equivalent to the $X_O^f = 1/3$ fluid composition. Because C-O-H fluid composition is relatively insensitive to f_{O2} it is actually more accurate to use X_O as an independent variable when you are interested in "max H2O" conditions.

```
Select buffer:

1 - aQFM, Holland & Powell, 298-1200K
2 - Maximum H2O content, 523-1273K, .5-30kbar
3 - constant f(O2)
4 - aQ-Ru-Cc-Tn-Gph, Holland & Powell
5 - ln(fO2) = a + (b + c*p)/t + d/t**2 + e/t**3
1
```

The f_{O2}/f_{CO2} buffers permitted here are those entered in the routine "fo2buf" in the file flib.f. It is easy to add new buffers to this routine, or by choosing option 5, you can specify your own buffer. Note that for option 5, p is the pressure in bar, t is the temperature in K, and the user is prompted for the values of the parameters a-e. The f_{O2} for many buffers can be adequately expressed as:

$$\ln f_{O_2} = \frac{-\left(\Delta H(T_{ref}, P_{ref}) - (T - T_{ref})\,\Delta S(T_{ref}, P_{ref}) + (P - P_{ref})\,\Delta V(T_{ref}, P_{ref})\right)}{RT}$$

in which case, for option 5, $a = -\Delta S/R$, $b = -(\Delta H + T_{ref}\,\Delta S - P_{ref}\,\Delta V)/R$, $c = -\Delta V/R$ and $d = e = 0$.

```
Modify calculated fO2 by a constant (Y/N)?
y
Enter constant in units of log10(fO2):
```

```
1
```

For some strange reason, petrologists are fond of defining f_{O2} by a constant (log) displacement relative to a buffer, e.g., QFM+1 or NNO-1. While I doubt the utility of this, the foregoing prompts permit it, specifically here the calculation would yield fluid speciation consistent with f_{O2} being one $\log_{10}$ unit above that of the quartz-fayalite-magnetite equilibrium.

While there is no lower limit on the $\log(f_{O2})$ of fluids in equilibrium with graphite, there is an upper limit, namely the f_{O2} of a graphite saturated C-O fluid. If the f_{O2} buffer specified for a calculation lies above this limit PeRpLeX writes a warning message and treats the fluid as a pure CO_2 fluid, regardless of the actual f_{O2} value. If you are interested in such fluid compositions it is better to do a calculation with $X_O^f = 1$.

```
Compute f(H2) & f(O2) as the dependent fugacities
(do not unless you project through carbon) (Y/N)?
n
```

For Method I calculations the response to the above prompt is always no.

```
Reduce graphite activity (Y/N)?
n
```

By responding yes to the above prompt it is possible to explore the effects of reduced (or increased graphite activity).

BEWARE, there is one catch to Method I calculations, if VERTEX is instructed to treat O_2 as a saturated component, then VERTEX will compute the μ_{O2} by adding the f_{O2} of the fluid to the free energy of the standard state entity with the lowest free energy for O_2. This should be the hypothetical ideal gas O_2, but in some cases there may be other entities in the thermodynamic data base with the O_2 composition, namely, some data bases may include O_2 buffers defined as a linear combination of oxides (Doc Sect 1.5), e.g., hematite - magnetite or magnetite + quartz - fayalite. These buffers invariably yield a lower standard state free energy for O_2 than the ideal gas standard state. It is therefore imperative that the user exclude any phases with the O_2 composition before calculations with VERTEX. If you have any doubts, you can always do the calculation and then look at the output to identify the stable O_2 composant. If it is something other than "O2" it should be excluded.

At present there is no provision in BUILD for the calculation of Schreinemakers diagrams as an explicit function of f_{O2}, this is because I believe that anything you can do with f_{O2} can be done better with X_O^f. If you really want to do calculations as a function of f_{O2} tell me and I will explain how to do them (it is possible with the current version of PeRpLeX).

6.2 P-T-X_O^f Diagrams: Method I

The practical aspects of computation of P–T–X_O^f diagrams requires little explanation because the variable X_O^f is treated by PeRpLeX in exactly the same way as the X_{CO2}^f variable. Indeed you can verify this for yourself by repeating the calculation done in Tut Sect 2, for a graphite saturated C-O-H fluid and because $X_O^f > 1/3$ fluids are essentially H_2O-CO_2 mixtures, the T-X_O^f and T-X_{CO2}^f topologies are virtually identical.

6.2.1 Fluid Components

The choice of fluid components for P-T-X_O^f diagrams is exactly as for computations with buffered f_{O2} (previous section); i.e., normally both H2O and CO2 are chosen as components of the saturated phase, O2 is chosen as a saturated component, and any entity other than ideal gas O2 with the composition O_2 must be excluded. The complete record of a BUILD session for a T–X_O^f diagram is in file `sample.8.`

6.2.2 Fluid Equations of State for P-T-X_O^f Calculations

The X_O^f variable is substituted for X_{CO2} automatically by PeRpLeX if the user chooses a fluid routine that supports it (i.e., routines 10-12, 16, 17, 19, 20, see file `README.COHSRK`). For graphitic (C-O-H fluids) rocks routines 10-12 are appropriate, 10 and 12 being preferable to 11. Routine 12 is a little more general in that it includes $O_{2,}$ a potentially important species in S-free fluids at **very** low graphite activities. If you wish to compute fluid speciation explicitly see files `README.COHSRK`, `README.SPECIES`, and `README.ISO.`

The prompts that follow the choice of fluid routine 12 are as follows:

```
Choose a buffer:
 1 - Pyrite + Pyrrhotite
 2 - Pyrrhotite
 3 - f(S2)
3
```

This prompt determines how the f_{S2} for the fluid is computed. Option 1 gives the f_{S2} in equilibrium with pyrite + pyrrhotite, option 2 gives the f_{S2} for a user specified pyrrhotite composition, and option 3 permits specification of a fixed f_{S2}.

```
Enter log10[f(S2)]:
-400
```

By choosing an extremely low f_{S2}, as done here, it is possible to use routine 12 for effectively S-free fluids.

```
Compute f(H2) & f(O2) as the dependent fugacities
(do not unless you project through carbon) (Y/N)?
n
```

As before, for Method I calculations the answer to the previous prompt is always no, and the response to the following prompt can be whatever the user desires.

```
Reduce graphite activity (Y/N)?
n
```

6.3 P-T-X_O^f Diagrams: Method II

In method II computations of graphite-saturated phase equilibria, the C-O-H fluid composition space is actually projected through carbon component into the O-H subcomposition. For such a projection to be possible in PeRpLeX it is necessary that the fluid composition be defined in terms of the components C, H_2, and O_2, instead of the default components CO_2, H_2O and O_2. Although this component transformation can be done in BUILD it is so tedious that I generally create a new data base file with the components C, H_2, and O_2 with the program CTRANSF, once this has been done the new data base file can used with BUILD and VERTEX.

6.3.1 Running CTRANSF

The prompts from CTRANSF are as follows:

```
Enter thermodynamic data file name (e.g. hp94ver.dat):
hp94ver.dat
Output will be written to file: ctransf.dat
```

i.e., the new thermodynamic data file will be named `ctransf.dat,` you can, of course, give it a more convenient name.

```
The data base components are now:
NA2O  MGO   AL2O3 SIO2  K2O   CAO   TIO2  MNO   FEO   O2    H2O   CO2
Transform them (Y/N)?
y
```

Because X_O^f is treated in the same manner as X_{CO2}^f in PeRpLeX, it is necessary to make the component transformation in such a way that H_2O becomes H_2 and CO_2 becomes O_2. This leads to the rather odd requirement that the original O_2 component must be transformed into C as the first transformation. Also despite the fact that I used O and H as components in my paper on phase diagram methods for graphitic rocks (Connolly 1994), the fluid routines in PeRpLeX require O_2 and H_2 as components.

```
Enter new component name (< 5 characters, left justified):
C
Enter old component to be replaced with C    :
O2
Enter other components (<12) in C     1 per line, <cr> to finish:
CO2

Enter stoichiometric coefficients of:
O2    CO2
in C     (in above order):
-1 1
C     =  -1.00 O2     1.00 CO2
Is this correct (Y/N)?
y
The data base components are now:
NA2O  MGO   AL2O3 SIO2  K2O   CAO   TIO2  MNO   FEO   C     H2O   CO2
Transform them (Y/N)?
y
```

Note that CTRANSF (and all other PeRpLeX programs) uses the new component as soon as it is created.

```
Enter new component name (< 5 characters, left justified):
O2
Enter old component to be replaced with O2   :
CO2
Enter other components (<12) in O2    1 per line, <cr> to finish:
C

Enter stoichiometric coefficients of:
 CO2   C
in O2    (in above order):
1 -1
O2    =   1.00 CO2   -1.00 C
Is this correct (Y/N)?
y
The data base components are now:
NA2O  MGO   AL2O3 SIO2  K2O   CAO   TIO2  MNO   FEO   C     H2O   O2
Transform them (Y/N)?
y
Enter new component name (< 5 characters, left justified):
H2
Enter old component to be replaced with H2   :
H2O
Enter other components (<12) in H2    1 per line, <cr> to finish:
O2

Enter stoichiometric coefficients of:
 H2O   O2
in H2    (in above order):
1 -.5
H2    =   1.00 H2O   -0.50 O2
Is this correct (Y/N)?
y
The data base components are now:
NA2O  MGO   AL2O3 SIO2  K2O   CAO   TIO2  MNO   FEO   C     H2    O2
Transform them (Y/N)?
n
```

For the sake of completeness you may want to change the name of the saturated phase variable in the new data file `ctransf.dat` from "X(CO2)" to "X(O)". **NOTE** that you can not use the transformed data file for P-T-X^f_{CO2} diagrams.

6.3.2 BUILD

To make a P-T-X^f_O calculation, run BUILD with ctransf.dat as the thermodynamic data file. The saturated phase prompt will become:

```
Calculations with a saturated phase (Y/N)?
The phase is:   FLUID
Its components can be: H2    O2
Its compositional variable is: X(O)
y
Enter number of components in the   FLUID
```

```
(1 or 2 for COH buffered fluids):
2
```

As with Method I, the number of components entered in response to the last prompt does not effect the way VERTEX does fluid speciation calculations, but it does determine which phases will be considered. Here if O2 is excluded neither carbonates nor oxidized phases will be included in the calculation, and if H2 is excluded any phase that contains H will be rejected.

The only other difference from normal P-T-X^f_{CO2} calculations is that in calculations for carbon-bearing systems it is essential that carbon be specified as a saturated component. At present there is no provision in the fluid speciation routines for the graphite-diamond transition, consequently PeRpLeX should not be used in the diamond stability field.

BEWARE, as with Method I, PeRpLeX will seek out the thermodynamic entities with the lowest standard state free energy to compute μ_{O2} and μ_{H2}. To be on the safe side it is wise (although possibly unnecessary) to exclude all ideal gas species other than H_2 and O_2, as well as any f_{O2} buffers that may be included in the thermodynamic data file.

Chapter 7

P-T PROJECTIONS FOR A SYSTEM INCLUDING A FLUID OF VARIABLE COMPOSITION

P-T-X^f_{CO2} and P-T-X^f_O diagrams are not particularly useful if one variable cannot be independently constrained. A useful, though initially difficult to understand, alternative is to compute a P-T phase diagram projection that shows phase equilibria for all possible fluid compositions as well as fluid absent conditions. The construction and theory of these diagrams with PeRpLeX is discussed in Connolly & Trommsdorff (1991, also Abart et al. 1992, Connolly 1994), in particular the Appendix of Connolly & Trommsdorff (1991) details some of the peculiarities that result from the pseudocompound approximation. Conventionally petrologists treat the compositional variable of the fluid phase as an explicit variable; however, in the calculation of variable fluid composition P-T projections the composition of the fluid is an implicit variable. In other words, the fluid is treated in the same way as a mineral solution and the components of the fluid are treated as thermodynamic components rather than saturated phase components. In the interests of demonstrating the value of the projections a simplified version of a field problem in graphitic metacarbonate rocks discussed by Alcock (1995) is presented here (beware I reconstructed this example from memory, so it may differ substantially from Alcock's analysis). The problem is as follows: In isothermal-isobaric metamorphism at a pelite-carbonate contact the assemblage phlogopite (phl) + diopside (di) + dolomite (do) + calcite (cc) occurs nearer to the pelite contact than the assemblage potassium feldspar (kf) + do + cc + tr. Since the metamorphism is isobaric and isothermal, the variation in mineral assemblages away from the contact can be reasonably assumed to be the result of a compositional gradient in the fluid between the water-rich pelite and the CO_2-rich carbonate. This implies that the assemblage kf + do + cc + tr must occur at higher X^f_O (see Tut Sect 6, or X^f_{CO2}) than does phl + di + do + cc at the P-T conditions for the metamorphism. The inevitable petrologic question is: what were these conditions? Because the solid phases are all very nearly stoichiometric the problem can be modeled in the system $KAlSi_3O_8$–CaO–MgO–SiO_2–C–O–H. To reduce the problem here to its most elementary aspects, note that the only other relevant phases are quartz (q) and forsterite (fo). Because the presence of graphite has minor influence on C-O-H fluid speciation within the stability field of calcite in siliceous rocks (i.e., the graphite-saturated fluid is very nearly an H_2O-CO_2 mixture) the fluid could be treated as a simple binary fluid, but a multispecies C-O-H fluid will be assumed here for the sake of generality and because it does not involve any additional complications.

A complete example of the BUILD prompts and responses for the calculation of a P-T projection for an H_2O-CO_2 fluid is in file `sample.8`

7.1 BUILD

To do a P-T projection for a system with a fluid of variable composition it is essential that the thermodynamic components are identical to the endmember components of the fluid phase. Thus in the present case, it is assumed that the user has already run CTRANSF (Tut Sect 6.3), to create a thermodynamic data file named **`ctransf.dat`** with the components C, O_2 and H_2

NOTE 1: To get VERTEX to do this calculation correctly (without computing high variance equilibria), it may be necessary to increase the "reliability level" to 3.

NOTE 2: This calculation may take 10-20 minutes on small computers (e.g. a Mac II).

An abridged listing of the prompts from BUILD follows:

```
 ...
Enter thermodynamic data file name (e.g. hp94ver.dat), left justified:
ctransf.dat
 ...
Specify type of calculation:
 0 - Composition diagram
 1 - Schreinemakers-type diagram
 3 - Mixed-variable diagram
1
 ...
The current data base components are:
NA2O  MGO   AL2O3 SIO2  K2O   CAO   TIO2  MNO   FEO   C     H2    O2
Redefine them (Y/N)?
y
```

Because phl and kf contain K_2O and Al_2O_3 in the same proportions it is possible to eliminate one component by defining the kf-composition as a component.

```
Enter new component name (< 5 characters left justified, blank to finish):
kf
Enter old component to be replaced with kf   :
K2O
Enter other components (<12) in kf    1 per line, <cr> to finish:
AL2O3
SIO2
Enter stoichiometric coefficients of:
K2O   AL2O3 SIO2
in kf    (in above order):
0.5 0.5 3
kf    =   0.50 K2O    0.50 AL2O3  3.00 SIO2
Is this correct (Y/N)?
y
Enter new component name (< 5 characters left justified, blank to finish):
 ...
Calculations with a saturated phase (Y/N)?
The phase is:   FLUID
Its components can be: H2    O2
Its compositional variable is: X(O)
n
```

Answer no to the above prompt!!!

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

For graphite saturated conditions it is necessary to saturate the system in carbon. Note that although the calcite is always stable in the rocks described by Alcock (1995), it is not possible to saturate the system in CAO component because VERTEX will not be projecting through the fluid components; thus the saturated CAO phase would always be a true CaO phase. However, after the calculation is done, the user can use PSVDRAW to exclude any equilibria that do not include calcite explicitly.

```
Select saturated components from the set:
NA2O  MGO   AL2O3 SIO2  kf    CAO   TIO2  MNO   FEO   C     H2    O2
How many saturated components (<8)?
1
Enter component names, left justified, one per line:
C
Use chemical potentials as independent variables (Y/N)?
n
Select thermodynamic components from the set:
NA2O  MGO   AL2O3 SIO2  kf    CAO   TIO2  MNO   FEO   H2    O2
How many thermodynamic components (<8)?
6
```

The user must enter the fluid components here, i.e., H2 and O2 for the present case, or H2O and CO2 for an H_2O-CO_2 fluid.

```
Enter component names, left justified, one per line:
kf
SIO2
CAO
MGO
H2
O2
**warning ver016** you are going to treat a saturated (fluid) phase component
as a thermodynamic component, this may not be what you want to do.
```

In this case, this is exactly what the user wants to do! **NOTE** that, in the computational option file, BUILD writes the components of the fluid phase first, and in the order in which they appear in the thermodynamic data file. This is important for bookkeeping in PeRpLeX. Thus, while it does not matter how they are entered here, if the computational option file is edited later, be careful to keep the fluid components in the same position as they were written originally by BUILD.

```
Constrained bulk compositions (y/n)?
n
```

You can, of course, do fixed bulk composition calculations by answering yes here.

```
Select fluid equation of state:
 ...
 10 - X(O) GCOH-fluid hybrid-EoS Connolly & Cesare 1993
 ...
10
```

For the present calculation routines 10-12 are valid choices, whereas for an H_2O-CO_2 fluid routines 0-6 and 18 are valid, and routines 15-17 can be used for carbon-free fluids.

```
Compute f(H2) & f(O2) as the dependent fugacities
(do not unless you project through carbon) (Y/N)?
y
```

As discussed in Tut Sect 6.3.2 it is essential to answer yes to the above prompt. The parenthetical comment is not strictly correct, i.e., if you are crazy enough to want to treat H-O or H-O-S fluids by this method then you would also answer yes here.

```
Reduce graphite activity (Y/N)?
n
```

If you want to reduce/increase graphite activity you can here.

```
Exclude phases (Y/N)?
y
 ...
```

Exclude all phases except the phases of interest (q, cc, dol, phl, tr, di, fo, kf, and graphite (gph)), the fluid endmembers H2 and O2, and the composants sio2, cao, mgo. In any case, be sure to exclude CH4, H2O, CO2, CO if you are doing calculations for a C-O-H fluid.

```
 ...
Consider solution phases (Y/N)?
y
```

At the very least, there is one solution in the system, i.e., the fluid, so answer yes to the above prompt.

```
Enter solution model file name (e.g. solut.dat), left justified:
solut.dat
 ...
Select phases from the following list,
one per line, left justified, <cr> to finish.
F           GCOHF       H2OM        M(A)
GCOHF
```

`solut.dat` usually contains at least two models for fluid "solution." In the version used here there are three, `F` is for an H_2O-CO_2 fluid, `GCOHF` is for a fluid with the endmembers H_2 and O_2, i.e., H-O, H-O-S, C-O-H, and C-O-H-S fluids; and H2OM which is a duplicate of GCOHF. The reason for including such duplicates is that they can be used to trick PeRpLeX into computing singular equilibria, or to make it easier to eliminate less interesting parts of the diagram with PSVDRAW (i.e., the user can create solution models for $X_O^f < 1/3$ and $X_O^f > 1/3$ C-O-H fluids, the models being identical except for their names and the compositional ranges considered). Here, H2OM yields a single composition, $X_O^f = 1/3$, which is the fluid composition at which pure dehydration equilibria have extrema in T-X_O^f and P-X_O^f, as such equilibria are of no importance in the present case only GCOHF is included for the calculation.

```
Calculate high variance phase fields (Y/N)?
n
```

In general, I answer no to this prompt at least for preliminary calculations. Answering yes can improve the reliability of the calculation (i.e., if you see incomplete invariant points or univariant fields, it usually helps to compute pseudounivariant equilibria, even if you later exclude them with PSVDRAW), and also helps in locating singular fields.

7.2 Binary Subdivision and Solution Models for a Fluid

Although it is a little out of place here, it may be helpful to describe the format of the solution model in `solut.dat` for the fluid phase. This format is discussed in detail in Doc Sect 4. The model used for the specific calculation here has the format:

```
GCOHF                                 solution name
1                                     isite
  2  0                                isp(1), ist(1)
O2       H2                           endmember names
  0  0                                endmember flags
 1.06  -.67      10.  1               subdivision ranges and model
  0  0                                iterm, iord
  0                                   msite
  0                                   ifix
```

with the explanatory comments to the right. The only difference between this model and that for an ideal binary (isp(1) = 1) single mixing-site (isite = 1) model, is that both the chemical and configurational site multiplicities are zero (i.e., `ist(1) = msite = 0`). This acts as a flag, which signals that VERTEX should compute the solution properties of the fluid from an internal subroutine, selected with BUILD, rather than the solution model in `solut.dat.` Thus, the solution model in `solut.dat` is used only to identify the fluid endmember compositions (line 2) and determine the subdivision scheme for generating pseudocompounds (line 4). In line 4 the parameters are, respectively, XMN(1,1), XMX(1,1), XNC(1,1), and IMD(1). The assignment IMD(1) = 1 in combination with the fact that solution is binary (ISP(1) = 2), indicates that VERTEX should generate pseudocompounds by symmetric transform subdivision (Fig 4.1b). For symmetric transform subdivision: XMN(1,1) is a stretching parameter that makes distribution of pseudocompounds more skewed towards the limits of the compositional range as XMN(1,1) approaches 1; if > 0, XMX(1,1) is the maximum concentration of the first endmember component, whereas if XMX(1,1) is < 0, its absolute value is the maximum concentration of the second endmember (in either case the corresponding minimum concentration is taken as 0); and the number of pseudocompounds to be generated is computed as 2(XNC(1,1)-1)-1.

Thus, the foregoing model will generate 17 pseudocompounds for the fluid with compositions from X^f_O=0.33 to X^f_O=1.00, with finer compositional resolution near these compositions. The reasons for choosing this scheme are: (i) is that it can be anticipated that the relevant carbonate equilibria occur on the CO_2-rich side of the X^f_O=1/3 composition; and (ii) it is desirable to have better compositional resolution near the X^f_O=1/3 and X^f_O=1 because low variance equilibria tend to occur in these regions.

Users should have no qualms about modifying or replacing the subdivision schemes currently in place in `solut.dat.` For example to obtain evenly spaced compounds at 5 mol % O intervals from X^f_O=0 to X^f_O=1, line 4 in the above model could be replaced by:

```
20.    0.0        20  1               subdivision ranges and mode
```

here the large value for the stretching parameter (XMN(1,1)) will yield evenly spaced compounds. Alternatively, the same thing can be accomplished by the scheme:

```
 0.00  1.00      .05  0               subdivision ranges and mode
```

IMD(1) = 0 indicates cartesian subdivision (Fig 4.1a), XMN(1,1) and XMX(1,1) are the minimum and maximum mole fractions of the first solution endmember (i.e., X^f_O), and XNC(1,1) is the compositional increment between adjacent pseudocompounds.

7.3 Output

The computed phase diagram projection is shown in Fig 7.1, and the isobaric T–X_O^f section (Tut Sect 6.3) in Fig 7.2 shows the fluid-saturated equilibria of Fig 7.1 at 4400 bar. An abridged summary of the equilibria shown in Fig 7.1, from the end of the print file is:

```
(pseudo-) invariant points are summarized below:

(   1-2) cc       dol      q        di       tr       kf       O295     O293
(   2-2) cc       dol      q        di       tr       kf       O293     O289
(   3-2) cc       dol      q        di       tr       kf       O289     O285
(   4-2) cc       dol      q        di       tr       kf       O285     O279
(   5-2) cc       dol      fo       di       tr       phl      O253     O247
(   6-2) cc       dol      fo       di       tr       phl      O247     O243
(   7-2) cc       dol      fo       di       tr       phl      O243     O239
(   8-2) cc       dol      fo       di       tr       phl      O239     O237
(   9-2) cc       dol      fo       di       tr       phl      O237     O235
(  10-2) cc       dol      fo       di       tr       phl      O235     O233
(  11-2) O299.1   q        fo       tr       dol      phl      kf       O297.7
(  12-2) cc       dol      phl      kf       tr       di       O293     O289
(  13-2) cc       dol      phl      kf       tr       di       O289     O285
(  14-2) cc       dol      phl      kf       tr       di       O285     O279
(  15-2) fo       di       dol      tr       kf       phl      O299.1   O297.7
(  16-2) O273     phl      q        dol      kf       tr       cc       O279
(  17-2) phl      q        dol      kf       tr       cc       O279     O285
(  18-2) kf       O299.1   q        fo       di       tr       dol      O2

(pseudo-) univariant equilibria are summarized below:

(   1-1) dol q = GCOHF(O2) di
(   2-1) cc dol q tr = di GCOHF(O295)
(   3-1) cc dol q tr = di GCOHF(O293)
(   4-1) cc dol q tr = di GCOHF(O289)
(   5-1) cc dol q tr = di GCOHF(O285)
(   6-1) cc dol q tr = di GCOHF(O279)
(   7-1) cc fo tr = dol di GCOHF(O253)
(   8-1) cc fo tr = dol di GCOHF(O247)
(   9-1) cc fo tr = dol di GCOHF(O243)
(  10-1) cc fo tr = dol di GCOHF(O239)
(  11-1) cc fo tr = dol di GCOHF(O237)
(  12-1) cc fo tr = dol di GCOHF(O235)
(  13-1) cc fo tr = dol di GCOHF(O233)
(  14-1) q dol phl = GCOHF(O299.1) fo tr kf
(  15-1) q dol phl = fo tr kf GCOHF(O297.7)
(  16-1) cc dol kf tr = phl di GCOHF(O293)
(  17-1) cc dol kf tr = phl di GCOHF(O289)
(  18-1) cc dol kf tr = phl di GCOHF(O285)
(  19-1) cc dol kf tr = phl di GCOHF(O279)
(  20-1) dol tr kf = fo di phl GCOHF(O299.1)
(  21-1) dol tr kf = fo di phl GCOHF(O297.7)
(  22-1) phl q cc = GCOHF(O273) dol kf tr
(  23-1) phl q dol cc = kf tr GCOHF(O279)
(  24-1) phl q dol cc = kf tr GCOHF(O285)
```

```
 (  25-1) q tr dol = GCOHF(O299.1) fo di
```

Note that the fluid pseudocompound names are made from the name of the first solution endmember (O2) followed by its mole fraction in the compound (Tut Sect 4.4). Thus O279 is the fluid composition X_O^f = 79 mole % O_2

Only a few aspects of the calculation are addressed here, a more detailed discussion is in the Appendix of Connolly & Trommsdorff (1991). There are two basic types of fluid-present univariant equilibria that appear in P-T projections: (i) true univariant equilibria (involving c+1 phases in non-degenerate systems), in which the fluid has a variable composition fluid; and (ii) singular univariant equilibria (involving c phases in non-degenerate systems), in which the fluid phase has a fixed composition if the other phases are stoichiometric (as in the present case).

7.3.1 True Univariant Curves

True (i.e., Type (i)) univariant equilibria correspond to invariant points in T–X_O^f diagrams. For example, in Fig 7.1, the true univariant equilibrium cc + fo + tr = do + di + Fluid, corresponds to the invariant point (7) in Fig 7.2 that defines the lower thermal stability of do + di in water-rich fluids. In establishing the fluid composition along such a univariant curve it is best to estimate fluid compositions from the pseudoinvariant points, e.g., at pseudoinvarint point (10) (in the above list and Fig 7.1) the fluid has an X_O^f = 34 mole % O, given by the average of the fluid pseudocompounds O233 and O235. In Fig 7.1, the true univariant equilibrium di = tr + q + do + cc (invariant point (2) in Fig 7.2) limits the stability of di + do assemblages in CO_2-rich (i.e., high X_O^f) fluid.

7.3.2 Singular Univariant Curves

Singular univariant equilibria correspond to P-T extrema in the univariant curves of T–X_O^f or P–X_O^f diagrams. For example, these two univariant equilibria mentioned above are related by the singular curve (dashed) 3 cc + tr = 4 dol + di + GCOHF(O260) that defines the P-T conditions of the maximum in the cc + tr = do + di T–X_O^f univariant field of Fig 7.2. The singular fluid composition can be computed from the stoichiometry of H_2 and O_2, i.e.,

$$X_O^f = \frac{\nu_{H_2}}{\nu_{H_2}+\nu_{O_2}}.$$

An obvious limitation of VERTEX is that it will not identify singular equilibria unless there is a pseudocompound with the singular fluid composition. Thus, in the present case VERTEX did not identify the 3 cc + tr = 4 dol + di + GCOHF(O260) singular curve in Fig 7.1, rather I computed the conditions for the singular curve using FRENDLY (one could also do this with VERTEX) and superimposed them on the P-T diagram. Comparison of Figs 7.1 & 7.2 reveals that all the additional singular equilibria, except those for the X_O^f composition, are not shown in Fig 7.2. However, the singular equilibria are unimportant in the context of the present problem, so I did not bother to compute them.

Singular curves may merge into true univariant curves at conditions known as singular points across which the stoichiometric coefficient of one phase in the true univariant curve changes sign. Even though VERTEX will not generally locate singular equilibria, it always possible to locate singular points by looking for such stoichiometric changes in the list of univariant equilibria. In the present calculation it can be seen by inspection that the phl + q + cc + dol + kf + tr + Fluid univariant curve has a singular point in the vicinity of the pseudoinvariant point (16). At pressures above this point the univariant reaction (22) is phl + q + cc = dol + kf + tr + Fluid, whereas below it the reaction (23) is phl + q + dol + cc = kf + tr + Fluid. It follows that the singular reaction is phl + 4.8 q + 1.2 cc = kf + 0.6 tr + 0.4 H_2 + 1.4 O_2 (i.e., $X_O^f = 0.778$) thus the real singular point probably occurs at lower pressure than pseudoinvariant point (16) ($X_O^f = 0.76$) and by topologic arguments it can be shown that the phl + q + cc = kf + tr +

Fluid($X_O^f = 0.778$) singular curve can only be stable at pressures below the singular point and temperatures above the phl + q + cc + dol = kf + tr + Fluid univariant equilibrium.

7.3.3 Graphite Stoichiometry (about as clear as mud)

The stoichiometries output by VERTEX do not take into account the amount of carbon in the fluid phase (because this varies continuously). If it is desired to know these stoichiometries at a specific condition the user can determine them from the output in conjunction with program COHSRK. For example, consider the output:

```
 (   2-1) cc dol q tr = di GCOHF(O295)

          Alpha(-.124, -.407, -.897, -.413E-01, 0.614, 1.00)
          Delta(  C    ) =-.938     (saturated composant=gph     )
          Delta(-V(j/b)) =-3.59     (dependent conjugate of P(bars) )
          Delta(S(j/k) ) = 87.1     (dependent conjugate of T(K)    )

  786.373      2000.00       788.419      2050.00
```

the indicated reaction is: 0.124 cc + .407 do + .897 q + .0413 tr = 0.614 di + 1.00 Fluid. At 786 K and 2000 bar, COHSRK indicates that the fluid has the atomic fractions: Y(C) = 0.31641, Y(H) = 0.03418 and Y(O) = 0.6491. In the limit of a binary H_2O-CO_2 mixture, $X_O^f = 0.95$ is equivalent to $X_{CO2}^f = 0.9487$ (Tut Sect 6), for which the atomic fractions would be: Y(C) = 0.31623, Y(H) = 0.03421 and Y(O) = 0.64956. Thus at this condition, a graphite-saturated fluid containing 0.95 mole O and 0.05 mole H, will contain 1.46353 mole C (i.e., 1/(Y(H)+Y(O))), whereas, in the binary limit, the fluid would contain 1.46248 mole C. The difference in these carbon contents must be made up by the consumption of graphite, i.e., the stoichiometric coefficient of graphite is 0.001 in the above reaction. This illustrates the generality that, in contrast to redox processes, dehydration-decarbonation reactions involve negligible amounts of graphite.

7.4 Alcock's Phase Diagram Problem

For users who are unfamiliar with P-T projections, probably the easiest way of solving the problem posed in this chapter is to compute a T-X_O^f or P-X_O^f diagram to establish which P-T univariant curves are of interest. Thus, referring to the T-X_O^f diagram of Fig 7.2 it can be seen that kf + cc + do + tr can only be stable within the shaded triangular region bounded by invariant points (1), (2) and (4), whereas phl + di + do + cc can only occur within the region bounded at low temperature by invariant points (7), (1) and (3). Thus for both assemblages to be stable at the same P-T condition, the T-X_O^f invariant point (7) must occur at temperatures below T-X_O^f invariant point (1). T-X_O^f invariant points (7) and (1) correspond to the cc + fo + tr = do + di + Fluid and cc + do + kf + tr = di + Fluid P-T univariant curves, and the minimum temperature for the kf + tr + Fluid, defined by T-X_O^f invariant point (4) corresponds to the phl + q + dol + cc = kf + tr + Fluid univariant curve. Consequently, the equilibrium P-T conditions for Alcock's assemblages must be within the shaded region of Fig 7.1. You could easily determine this by first instructing PSVDRAW to show only equilibria involving the assemblage cc + do + di and then the assemblage cc + kf + tr + do; and then superimposing the two stability fields. Note that this would not work if you asked PSVDRAW to show the stability field of phl + cc + do + di, because phl is an indifferent phase (i.e., has a zero stoichiometric coefficient) in the equilibrium that limits the stability of di + do.

It may be useful to note that if this calculation is done with Berman's data a vastly different topology is derived, because Bermans data predicts that the right hand side of the fluid-absent reaction kf + tr = q + phl + di is stable within much of the P-T region shown in Fig 7.1. Thus, in the context of the present problem it appears that only Holland & Powell's data is consistent with Alcock's observations.

7.5 Determination of Singular Equilibria: Program STOICH

Usually I locate singular equilibria by using $T{-}X_O^f$ sections, but another method is the PeRpLeX program STOICH. At present all STOICH does is determine all possible singular equilibria among a collection of phases in which all the phases are stoichiometric except the fluid. In cases where non-stoichiometric phases are present the stoichiometry of a singular reaction and the singular fluid composition are no longer fixed; hence I have not bothered to improve STOICH beyond its present primitive state, but it would not require much to make STOICH determine the stable P-T condition. STOICH reads a data file named `stoich.dat` that has the following format:

```
3                        ICP
H2       O2              FLUID COMPONENT NAMES
Fo                       PHASE NAME
0.0 2.0 1.0 31.0 0.0     COMPOSITION VECTOR
Cc
1.0 0.0 0.0 0.0 1.0
Di
1.0 1.0 2.0 0.0 0.0
Do
1.0 1.0 0.0 0.0 2.0
Tr
2.0 5.0 8.0 1.0 0.5
Q
0.0 0.0 1.0 0.0 0.0
```

In line 1, ICP is the number of non-fluid components. Line 2 lists the names of the volatile components (format a8,1x,a8). The following lines are the name for each phase (other than the fluid), and a composition vector for the phase. The order in which the user enters the component non-fluid components is immaterial (provided it is kept the same for all the phases), but the fluid components must be entered last and in the order in which they are specified on line 2. In the above example, the composition vectors are for CaO, MgO, SiO_2, H_2 and O_2, these compositions are for the CaO-MgO-SiO_2-C-O-H system after projection through graphite.

STOICH determines the stoichiometries of all possible reactions between < ICP + 1 of the non-fluid phases (these are the univariant equilibria of $T{-}X_O^f$ diagrams) and in each case determines if the reaction is a possible singular equilibrium. The output from STOICH for the above data file is:

```
the (Fo,Cc) singular composition is x(O2 ) =  1.000
0.500     -.500        0.     -1.00
the (Fo,Di) singular point does not exist.
0.375     -.625     0.125     -1.00
the (Fo,Do) singular composition is x(O2 ) = 0.7778
-1.50      2.50     -.500     -1.00
the (Fo,Tr) singular composition is x(O2 ) =  1.000
   0.     0.500     -.500     -1.00
the (Fo,Q ) singular composition is x(O2 ) = 0.6000
-3.00      4.00      1.00     -1.00
the (Cc,Di) singular point does not exist.
-.231     -.308     0.154     -1.00
the (Cc,Do) singular composition is x(O2 ) = 0.3333
-.600     -.800     0.400     -1.00
the (Cc,Tr) singular composition is x(O2 ) =  1.000
   0.     0.500     -.500     -1.00
the (Cc,Q ) singular composition is x(O2 ) = 0.7500
 1.50      3.25     -1.25     -1.00
```

```
the (Di,Do) singular point does not exist.
-.455     -.364     0.182     -1.00
the (Di,Tr) singular composition is x(O2 ) =  1.000
 1.00      2.00     -2.00     -1.00
the (Di,Q ) singular composition is x(O2 ) = 0.9048
 8.00      13.0     -11.0     -1.00
the (Do,Tr) singular composition is x(O2 ) =  1.000
-.333     -.667     0.667     -1.00
the (Do,Q ) singular composition is x(O2 ) = 0.6842
0.667     -1.67      3.67     -1.00
the (Tr,Q ) singular composition is x(O2 ) =  1.000
0.667      1.33     -.333     -1.00
```

Each equilibrium is identified by those phases not present, and is followed by the stoichiometric coefficients of the phases in the same order as the phases are entered in the data file. Thus, the line:

```
the (Fo,Q ) singular composition is x(O2 ) = 0.6000
-3.00      4.00      1.00     -1.00
```

indicates that the reaction 3 cc + tr = 4 di + do is a possible singular reaction.

Chapter 8

THERMOBAROMETRY

Thermobarometry and estimation of fluid composition from mineral equilibria is done almost invariably by an inverse approach in which it is assumed that observed mineral compositions represent stable equilibrium compositions. These mineral compositions are then used to make activity corrections to compute the displacement of equilibria in some chemical subsystem of the rock. Drawbacks of this method are that it provides no test for the equilibrium assumption and that the reactions corresponding to the equilibria in the chemical subsystem often bear little resemblance to actual metamorphic processes. PeRpLeX provides a basis for an alternative approach in that it can be used to compute equilibria for the full chemical system of interest, or a close approximation thereof. The predicted and observed mineral assemblages can then be compared to estimate conditions of equilibration. This approach has the advantages that it provides a rigorous test for consistency between the observed mineral compositions and the thermodynamic models used to describe mineral behavior, and that the computed reactions correspond to those observed in nature.

This chapter presents two problems from diploma theses done at the ETH to illustrate how PeRpLeX can be used for thermobarometry.

8.1 Cima Lunga Garnet Schists, Wahl (1995)

Wahl (1995) observed microinclusion assemblages of epidote + margarite + anorthite + kyanite + quartz included within garnets from the Cima Lunga garnet schists. In these assemblages kyanite and quartz are essentially pure and epidote, margarite and anorthite are effectively binary solutions with the compositions $cz_{92\pm2}$, $pa_{11\pm2}$ and $an_{86\pm4}$. Assuming these assemblages represent relicts of an early equilibrium, the P-T conditions can be estimated from the Na_2O-CaO-Al_2O_3-FeO-H_2O-O_2 phase diagram.

8.1.1 BUILD

The calculation reproduced here was done with the following specifications: (i) thermodynamic data from hp94ver.dat file; (ii) saturation with a pure H_2O fluid; (iii) saturation with SiO_2 and Al_2O_3, i.e. quartz + aluminosilicate; (iv) CaO-Na_2O-FeO-O_2 as thermodynamic components; (v) fluid routine 5 (Holland & Powell 1991); (vi) compound zo was excluded; (vii) solution models EpCz (epidote), MaPa (margarite) AnPl (anorthite), AbPl (albite), Gt (garnet), T (talc), Chl (chlorite) from solution model file solut.dat; (viii) pressure is in the range 6-12 kbar, and temperature 860-1000 K; and (ix) high variance equilibria must be computed.

8.1.2 Thermobarometric Analysis and PSVDRAW

Thermobarometric analysis can be done with PeRpLeX at two different levels. At a low level (Level I) it is possible to pose the question as to whether the observed paragenesis is predicted to be stable within the model system. Once this has been confirmed, the analysis can be refined (Level II) to determine the conditions at which the observed and predicted mineral compositions match.

8.1.2.1 Level I

The stability field of margarite + epidote + anorthite (water, quartz, and kyanite are saturated phases) can be determined from the plot generated by PSVDRAW with the following dialog:

```
Modify the default plot (y/n)?
y
Modify default drafting options (y/n)?
n
Restrict phase fields (y/n)?
y
Suppress high variance equilibria (y/n)?
n
Show only with assemblage (y/n)?
y
Enter the name of a phase present in the fields
(left justified, <cr> to finish):
EpCz
Enter the name of a phase present in the fields
(left justified, <cr> to finish):
MaPa
Enter the name of a phase present in the fields
(left justified, <cr> to finish):
AnPl
Enter the name of a phase present in the fields
(left justified, <cr> to finish):

Show only without phases (y/n)?
n
Show only with phases (y/n)?
n
```

The resulting plot (Fig 8.1) shows that the assemblage is predicted to be stable, and that it is stable within a quadrilateral region of P-T space. Consequently, a Level II refinement can be justified. Note that because MgO is present in the rock (in garnet), but is absent from the inclusion assemblages, the addition of MgO component might reduce the Ma + Ep + An Level I stability field by stabilizing garnet. Fluid composition is also a potential variable that could be considered for Wahl's problem (it was for a similar problem addressed by Connolly et al. 1994).

8.1.2.2 Level II

Level II refinement consists of finding the conditions where the closest agreement between the observed and predicted mineral compositions. Generally the best approach for this is to instruct PSVDRAW to determine that stability field for a specific composition, or range of compositions, for each solution, while the compositions of the remaining solutions are unspecified. If an assemblage consists of p phases, then it is possible to determine at least p stability fields, and the region of overlap of these fields gives the range of conditions where all the predicted and observed compositions match. In the example illustrated in Fig 8.1, the dashed ellipses span the stability fields (determined by PSVDRAW, as above) of the assemblages: (1) {MaPa + EpCz + ab11 + ab17} (2) {MaPa + cz90 + cz95 + AnPl} and (3) {pa8 + pa12 + EpCz + AnPl}. Because the assemblage Ma + Ep + An is divariant in the projection (within the degenerate subcomposition $CaO–Na_2O–Fe_2O_3$) each of these assemblages is stable along a line in P-T space; where the composition of plagioclase is ab14 for assemblage (1), that of epidote is cz92 in (2), and that of margarite is pa10 in (3). As the three ellipses do not overlap it can be concluded that there is no condition where margarite + epidote + anorthite have the compositions ab14 + pa10 + cz92. The source of the discrepancy being (neglecting model error) that either the anorthite content of AnPl should be lower or the pa content of MaPa higher. The best (subjective) estimate for equilibrium conditions is then the smallest ellipse (shaded in Fig 8.1) drawn so as to overlap all three stability fields. The composition of the minerals at the the center of this ellipse can be estimated from the pseudo-invariant points to be ab8 + pa17 + cz92; the discrepancy in predicted and observed compositions is thus almost certainly not statistically significant.

The foregoing analysis was somewhat streamlined in that 2 pseudocompound compositions were specified for each assemblage. A more rigorous approach, which would give a clear picture of the role of compositional error, would be to determine the stability fields of the assemblages: (1) {MaPa + EpCz + ab11} (2) {MaPa + EpCz + ab17} (3) {MaPa + cz95 + AnPl} (4) {MaPa + cz90 + AnPl} (5) {pa8 + EpCz + AnPl} (6) {pa12 + EpCz + AnPl}. In this case the combined stability fields of assemblages (1) & (2), (3) & (4), and (5) & (6) would give the region in which anorthite, epidote, and margarite have the compositions in the range $X_{an} \approx$ 8-20 mole %, $X_{cz} \approx$ 88-98 mole %, and $X_{pa} \approx$ 6-14 %; ranges that are probably more representative of the compositional uncertainties for the natural paragenesis.

8.2 Cima Lunga Gneisses, Fixed-Activity Method, Grond (1995)

Grond (1995) describes coronas of plagioclase (an_{30}) and orthopyroxene (en_{68}) developed between kyanite, quartz, and garnets ($gr_{11}py_{27}$ - $gr_{8}py_{38}$) (none of the minerals show compositional zoning). This analysis could be done as in the previous example for the quartz + kyanite-saturated system Na_2O–CaO–MgO–FeO–SiO_2–Al_2O_3, but instead a simpler but less rigorous fixed-activity approach is demonstrated here. Fixed-activity methods involve the premise that one or more observed mineral compositions are those of a relict equilibrium. In the present case, if this is assumed for plagioclase, then Na_2O can be eliminated as a component, and, after projection through SiO_2 and Al_2O_3, it is also becomes possible to project through CaO component so that the analysis can be done with just two thermodynamic components, MgO and FeO. Basically this is a trick to get VERTEX to compute the composition of the orthopyroxene and garnet in equilibrium with the specified plagioclase. The catch being that the Level I analysis is no longer possible, since the user tells (rather than asks) VERTEX what the plagioclase composition is. To some extent the predicted compositions of the garnet and orthopyroxene provide a test for the validity of the analysis.

8.2.1 Fixed-Activity Corrections with FRENDLY

There is no provision for fixed-activity corrections within VERTEX; thus it is necessary to make the activity correction to the anorthite endmember of plagioclase in the thermodynamic data file. This can be done using either ACTCOR or FRENDLY, the latter is more difficult but will be illustrated here.

The abridged dialog from FRENDLY follows:

```
Enter the thermodynamic data file name, left justified, < 15 characters
(e.g. hp94ver.dat):
hp94ver.dat
 ...
Choose from following options:

 1) calculate equilibrium coordinates for a reaction.
 2) calculate thermodynamic properties for a phase or reaction relative to
    the reference state.
 3) calculate change in thermodynamic properties  from one p-t-x
    condition to another.
 4) create new thermodynamic data file entries.
 5) quit.
```

```
With options 1-3 you may also modify thermodynamic data,
modified data can then be stored as a new entry in the thermodynamic data
file.
2
```

The user could respond with 1-3 here and below, for option 1 the user would just specify a reaction with one phase.

```
Calculate thermodynamic properties for a reaction (y/n)?
n
Calculate thermodynamic properties for phase:
an
Enter activity of: an       (enter 1.0 for H2O or CO2):
0.69
```

Non-ideal solutions generally have P-T dependent activity composition relations you can put these in explicitly by modifying the phase properties. Alternatively, as done here, you can specify a fixed activity considered to be reasonable at the conditions of interest. The value 0.69 was computed with the PeRpLeX auxilliary program GTPL at 6000 bar and 873 K.

```
write a properties table (Y/N)?
n
```

By answering yes here you can tabulate thermodynamic properties as a function of P–T–X conditions, and then contour these with PSCONTOR.

```
Enter p(bars) and t(k) (zeroes to quit):
1 298.15
```

The values entered above are immaterial.

```
At   298.15    k and   1.00000    bar:
     G(kj)   = ...
Modify or output thermodynamic parameters of a phase (y/n)?
y
Do you only want to output data (y/n)?
y
```

The user would enter no above, to add in a P-T dependent activity correction.

```
Output reaction properties (y/n)?
n
Select phase to modify or output:
       1) an
1
Enter a name (<8 characters left justified) to distinguish the modified
version of an      . WARNING: if you intend to store modified data
in the data file this name must be unique.
an30
```

BEWARE by doing this the user makes a new entry in the thermodynamic data file `hp94ver.dat.` If you forget about this entry (i.e., if you do not delete it after you are done) you may confuse other users of the same file, or yourself, in subsequent calculations (e.g., the activity corrected anorthite an30 will always be more stable than the true anorthite endmember).

```
Enter p(bars) and t(k) (zeroes to quit):
0 0
Choose from following options:
 1) calculate equilibrium coordinates for a reaction.
  ...
 5) quit.
5
```

8.2.2 BUILD

The calculation reproduced here was done with the following specifications: (i) thermodynamic data from hp94ver.dat file as modified above; (ii) no fluid phase; (iii) saturation with SiO_2, Al_2O_3, and CaO, i.e. quartz + aluminosilicate + activity-corrected anorthite; (iv) MgO and FeO as thermodynamic components; (v) solution models E (orthopyroxene en-fs), GrPyAl(B) (ternary garnet), Crd (cordierite), O (olivene), Sp (spinel sp-hc), HeDi (clinopyroxene di-hed) from solution model file solut.dat; (vi) pressure is in the range 2-8 kbar, and temperature 673-873 K; and (vii) high variance equilibria must be computed.

8.2.3 Level II Thermobarometric Analysis

After doing the calculation outlined above with VERTEX, the user obtains the diagram shown in Fig 8.2b by instructing PSVDRAW to show only equilibria involving the assemblage orthopyroxene (E) + garnet (GrPyAl(B) or Gt). The resulting Opx + Gt stability field should not be confused with a Level I stability field because the phase compositions and locations of (pseudo-) univariant equilibria are dependent on the plagioclase composition specified for the calculation. Since the plagioclase composition was probably P-T dependent, it follows that the equilibria in Fig 8.2b are only thermodynamically consistent at the one P-T condition where the plagioclase equilibrated.

The Level II analysis of the can be done by recognizing that pseudouninvariant curves of Fig 8.2a indicate the compositions of coexisting garnet + orthopyroxene (+ plagioclase + kyanite + quartz). Because orthopyroxene has only one compositional variable, the pseudounivariant equilibria involving two opx compounds can be interpreted simply as contours of the opx compositions (as in Fig 8.2b). Pseudounivariant equilibria involving two garnet compounds define the boundaries of polygonal P-T regions in which one garnet pseudocompound is stable. Because garnet has two compositional degrees of freedom there is no direct relation between these boundaries and compositional contours, although it is possible to discern a general trend of decreasing grossular content with decreasing pressure, and of increasing pyrope-content with increasing enstatite-content in opx. The garnet pseudocompound composition will most nearly match the true solution composition at the centroid of each polygon. Thus, Grond's (1995) $gr_{11}py_{27}$ garnet should occur near the center of the g11p27 polygon, whereas his more pyrope-rich compositions should lie along a trend toward the upper edge of the g5p38 polygon. The range of predicted Opx compositions along this trend can be estimated from the ferrosilite isopleths to be en_{68}–$en_{73,}$ in reasonable agreement with the observed composition of $en_{68.}$ This agreement supports the assumption that the coronas represent an equilibrium that occurred at roughly 7000 bar and surprisingly low temperatures (773-823 K). Before accepting this result it would be advisable to determine how sensitive the results are to variations in anorthite activity.

Chapter 9

CALCULATIONS FOR FIXED BULK COMPOSITIONS

VERTEX was designed to compute phase diagrams for all possible compositions of a thermodynamic system, but it is also possible to use VERTEX to compute phase equilibria for specified bulk compositions of a system. In this mode VERTEX outputs the same kind of information as free energy minimization programs. Users should be aware that free energy minimization programs can treat much more complex solution behavior, so such programs may be better suited for some fixed-bulk composition calculations, particularly those involving complex aqueous solutions or melts. However, VERTEX has the advantage of permitting saturation constraints, and some other features, which are generally not supported in free energy minimization programs.

Users should also be aware that a key assumption in any fixed-bulk composition calculation is that the system is in overall equilibrium (an assumption which is of much less importance in phase diagram methods). This is rarely true in crustal rocks because: (i) minerals often show compositional zoning and (ii) often there are relicts of several different equilibria present in the same rock. Furthermore rocks are often heterogeneous on so fine a scale that it is not possible to define a representative bulk composition. Despite these caveats, such calculations are surprisingly useful. Because they are easy to interpret, they provide a means of understanding the significance of their more complex brethren, phase diagrams. The innumerable pseudo-sections published by Powell, Holland, and coworkers bear grim testimony to this. Fixed-bulk calculations can also be useful in thermobarometry because many assemblages have very restricted stability fields for a specific composition.

This chapter presents details the calculation of a $T-X^{f}_{CO2}$ diagram for pelite composition in the KFMASHC system.

9.1 BUILD

Most of the prompts for BUILD are answered as for any other type of calculation. An abridged BUILD dialog follows:

```
 ...
Enter thermodynamic data file name (e.g. hp94ver.dat), left justified:
hp94ver.dat
Specify type of calculation:
  0 - Composition diagram
  1 - Schreinemakers-type diagram
  3 - Mixed-variable diagram
1
```

Any type of calculation can be done for fixed-bulk compositions.

```
Calculations with a saturated phase (Y/N)?
The phase is:   FLUID
Its components can be: H2O   CO2
Its compositional variable is: Y(CO2)
```

```
y
Enter number of components in the   FLUID
(1 or 2 for COH fluids):
2
Calculations with saturated components (Y/N)?
y
Select saturated components from the set:
NA2O  MGO   AL2O3 SIO2  K2O   CAO   TIO2  MNO   FEO   O2
How many saturated components (<8)?
3
Enter component names, left justified, one per line:
SIO2
AL2O3
K2O
Use chemical potentials as independent variables (Y/N)?
n
Select thermodynamic components from the set:
NA2O  MGO   CAO   TIO2  MNO   FEO   O2
How many thermodynamic components (<8)?
2
Enter component names, left justified, one per line:
FEO
MGO
```

If you think about it long enough (5 seconds?) you will realize that specification of saturated components is a form of compositional constraint; and is, in fact, redundant if you are also going to specify the amounts of the saturated components. There are still two reasons to specify saturated components: (1) you can do a calculation where you only specify the amounts of the thermodynamic components; and (2) it makes the computation simpler, so you can specify a larger total number of chemical components. The disadvantage here is that the phase diagram plot will not show the aluminosilicate, muscovite, and K-feldspar phase boundaries.

```
Constrained bulk compositions (y/n)?
y
How many bulk compositions (< 21)?
1
```

Multiple compositions are possible, but the results get difficult to interpret for any calculation other than a composition diagram.

```
Skip equilibria that do not effect the bulk compositions (y/n)?
y
```

It is imperative to answer yes to the above prompt. Otherwise the calculation will mostly involve irrelevant equilibria.

```
Only specify thermodynamic components (y/n)?
n
Enter molar proportions of the components:
  MGO   FEO   SIO2  AL2O3 K2O
in composition   1:
 0.078 0.0573 0.9754 0.245 0.0356
```

By answering yes to the above prompt, it would be possible to do a calculation in which none, or only some, of the saturated components are specified. An example where this might be appropriate would be a when a series of qtz + mu/kf + aluminosilicate rocks have variable proportions of the saturated components SiO_2–Al_2O_3–K_2O but relatively constant FeO-MgO proportions. All the rocks would then have the same composition in the thermodynamic composition space. At present BUILD does not permit the user to specify saturated phase components (i.e., H_2O and CO_2 here), because usually in petrologic problems the bulk analysis does not include the fluid that is presumed to have been present in the system. However, the computational option file can be modified so that VERTEX will include the fluid components as part of the bulk composition.

NOTE if you enter fictitious bulk compositions be careful to avoid specifying a degenerate compositions (usually simple proportions), e.g. for a calculation in the system MgO-SiO_2 specification of the composition 0.5 mol MgO 0.5 mole SiO_2 would lead to problems if enstatite were stable, since PeRpLeX would be unable to decide if the stable assemblage should be enstatite + quartz or enstatite + forsterite (PeRpLeX would assume both were stable).

The user selects: fluid routine 5, X^{f}_{CO2} (0-1) as the x-axis variable, temperature (673-923 K) as the y-axis variable, and a pressure for the section of 4000 bar. The user then opts to treat solutions, using the solution model data file `solut.dat,` and selects the solution models: `Chl, Crd, Gt, Bio, St, M, E, Ctd,` and `T` (chlorite, cordierite, garnet, biotite staurolite, magnesite-siderite, orthopyroxene, chloritoid, and talc, respectively).

```
Calculate high variance phase fields (Y/N)?
y
```

If the system involves solutions, it is essential to calculate high variance phase fields because it is probable that these may determine when phases appear or disappear.

9.2 Print Output

For a fixed-bulk composition computation the print output includes the compositional and modal information for every relevant assemblage in addition to the normal VERTEX output.

The first set output for type 1 and type 3 calculations is always for the minimum values of all selected variables. In the present case, the first mode, reproduced below, is at T = 673 K, P = 4000 bar, and X_{CO2} = 0 mol.

```
Composition   1 is bounded by the assemblage:
 mc24     cl57-24
in the thermodynamic composition space.

             mol %      wt %     vol %
 mc24         7.67     15.43     12.75
 cl57-24      2.12     10.73     10.68
 q           75.79     37.52     41.09
 ky           5.64      7.53      5.95
 mu           8.77     28.79     29.52

             mol %      wt %
    FEO       4.89      5.69
    MGO       3.60      2.35
    SIO2     61.21     59.51
    AL2O3    15.37     25.36
    K2O       2.23      3.40
    H2O      12.69      3.70
```

```
    CO2       0.00      0.00

Reference state density (g/cm3):  2.900
( 4000.00      673.000           0.            0.           0.     )
```

This output indicates that at the specified conditions the rock would be composed of 12.75 vol % chloritoid (X_{Mg}=0.24), 10.68 vol % chlorite (X_{Mg}=0.57, $X_{tschermaks}$=0.76), 41.09 vol % quartz, 5.95 vol % kyanite, and 29.52 vol % muscovite. Note that mineral modes and the bulk density are computed using reference state densities; thus the (minor) effects of mineral expansivity and compressibilities are not incorporated (although they are for the computation of phase equilibria).

VERTEX also outputs a back-calculated chemical composition for each assemblage. If a component is not specified in the bulk composition, but is present as a saturated component then VERTEX determines the minimum amount of this component necessary to maintain saturation (i.e., the amount of the saturated components present in the phases whose abundances are determined by the specified components). If the user has specified that a component is saturated, but the bulk composition is, or becomes, inconsistent with this constraint, then the amount of the corresponding composant will be negative and VERTEX will write a warning message following the mode. **BEWARE** VERTEX will continue with phase diagram calculations regardless of whether the composition and saturation constraints are consistent, so the user is strongly advised to scan the print output for such warnings.

The final line indicates, respectively, the P, T, saturated phase composition, and the first and second independent chemical potentials (the last three values are only significant if the variables are being used in the calculation) when the mode was computed.

9.3 Plot Output

If an assemblage involves solutions in a real system then the modes of the minerals will vary continuously with the independent intensive variables of the system. In VERTEX this continuous variation is replaced by a stepwise changes defined by pseudo-univariant equilibria. Thus, provided the user has entered only a single bulk composition and has instructed VERTEX to compute only those equilibria that effect the bulk composition (as above), within each region bounded by (pseudo-)univariant curves of a Schreinemaker's projection there is only one pseudocompound assemblage possible. The T-X^f_{CO2} projection for the present problem is shown in Fig 9.1. By analysing such a grid, given the identity of the stable assemblage at some point within it, it is possible to determine the stable assemblages in every region of the grid. Alternatively, one can refer to the mineral proportions and P-T-X^f_{CO2} conditions reported in the print file to determine the mineral modes as a function of the intensive variables. Unfortunately, because I have not yet thought of a way of organizing the information in the print file this can be fairly tedious. PSVDRAW can be used as a shortcut in this kind of analysis in several different ways. For example, Fig 9.1b, which shows the stable phase assemblages represented in Fig 9.1a, was constructed by requesting PSVDRAW to construct diagrams showing equilibria involving one solution. The region encompassed by the equilibria in each of these diagrams corresponds to the stability field of the specified solution, when these fields are outlined and superimposed upon eachother Fig 9.1b is obtained (in Fig 9.1b thick lines indicate univariant fields and thin lines represent higher variance phase field boundaries). In the case of systems with saturated components, the complete assemblages can be determined by constructing a second diagram, such as Fig 9.1c, that shows the stability of the phases determined by the saturation constraints.

When a diagram is constructed as described above, if two fields share a common boundary, then the boundary must be a univariant curve (these can be determined from topology or by instructing PSVDRAW to show only low variance fields and superimposing these fields on the diagram). However in contrast to a phase diagram projection, the univariant curves in such diagrams, which are phase diagram sections, may terminate at either an equilibrium of higher or lower variance. The only general rule being that the number of phases in adjacent fields (regardless of dimension) must always differ by one.

9.4 TERTEX, a Program for Fixed-Bulk Compositions

The kinds of problems that can be done with fixed bulk compositions can be much more complex than those done normally with VERTEX. This means that the default dimensioning of arrays in VERTEX may be inadequate for some problems. To save the user the trouble of redimensioning VERTEX, there is a second PeRpLeX program named TERTEX. TERTEX determines stable phase assemblages by a brute force algorithm that requires much less memory.

Except for the algorithm and one interactive prompt TERTEX is identical to VERTEX (i.e., the user sets the problem up using BUILD, etc.). TERTEX can be run in two ways determined by the users response to the TERTEX prompt:

```
enter the assemblage yourself (y/n)?
```

If the user answers no, the program behaves identically to VERTEX (although it is considerably slower in the initial stage of the calculation).

If the user responds yes, the user must then input the assemblage that is stable at the minimum values for all the variables of the requested (in the computational option file) phase diagram section. By doing this the user is able to bypass the inefficient part of TERTEX's algorithm. Thus, once the user has computed one phase diagram section with VERTEX or TERTEX, he/she/it can make use of her/his/its knowledge of the stable assemblages in a system to make calculations very efficiently with PeRpLeX.

As an example, suppose that after making the T-X_{CO2}^{f} section discussed above with VERTEX, the user attempts to make a P-T section for X_{CO2}^{f} = 0 for P = 4000-10000 bar and T = 673-973. For the sake of argument suppose the user first tries this with VERTEX, but he finds that the saturation constraints are no longer valid, and when he relaxes the saturation constraints VERTEX responds that its current dimensioning is inadequate. Rather than redimensioning VERTEX (a painful excursion into FORTRAN), the user can now use TERTEX given that he knows that the stable assemblage in the system at X_{CO2}^{f} = 0, 673 K, and 4000 bar is mc24, cl57-24, q, ky, and mu. Because TERTEX asks for the phase indices (which may vary if the user adds phases or changes subdivision schemes) the user should responds yes to the prompt:

```
output phase indices (y/n)?
y
```

Upon which TERTEX outputs a list (abridged here) like:

```
    1 H2O          2 CO2          3 kal3o        4 kalo2        5 k2o          6 sio2
    6 sio2         7 al2o3        8 mu           9 kf          10 san         11 kals
   11 kals        12 lc          13 dia         14 pyhl        15 kao         16 and
   16 and         17 ky          18 sill        19 cor         20 q           21 bq
 ...
  186 cl78-99    187 cl85-99    188 cl92-99    189 cl7-0      190 cl14-0     191 cl21-0
  191 cl21-0     192 cl28-0     193 cl35-0     194 cl42-0     195 cl50-0     196 cl57-0
 ...
  466 py60       467 py65       468 py70       469 py75       470 py80       471 py85
  471 py85       472 py90       473 py95
```

The user can then identify the indices for his assemblage (i.e., 20 for q, 17 for ky, etc), and enter them in response to the final TERTEX prompt:

```
enter phase indices
```

There are many ways of using TERTEX efficiently, the key to all of them is finding some way, by hook or crook, of identifying the initial assemblage. Usually I do this by solving some very simplified problem (e.g., by excluding solutions, or using very restricted subdivision schemes) at the initial condition with VERTEX.

Chapter 10

CALCULATIONS WITH VARIABLE CHEMICAL POTENTIALS, FUGACITIES AND ACTIVITIES

Oops, hold your horses! Sorry, not yet written. For some help see examples 6 and 7 in the examples folder/directory. Well obviously I've had it with writing this stuff. Stay tuned, some year I may revise the last 5 chapters so they can be read by humans.

Chapter 11

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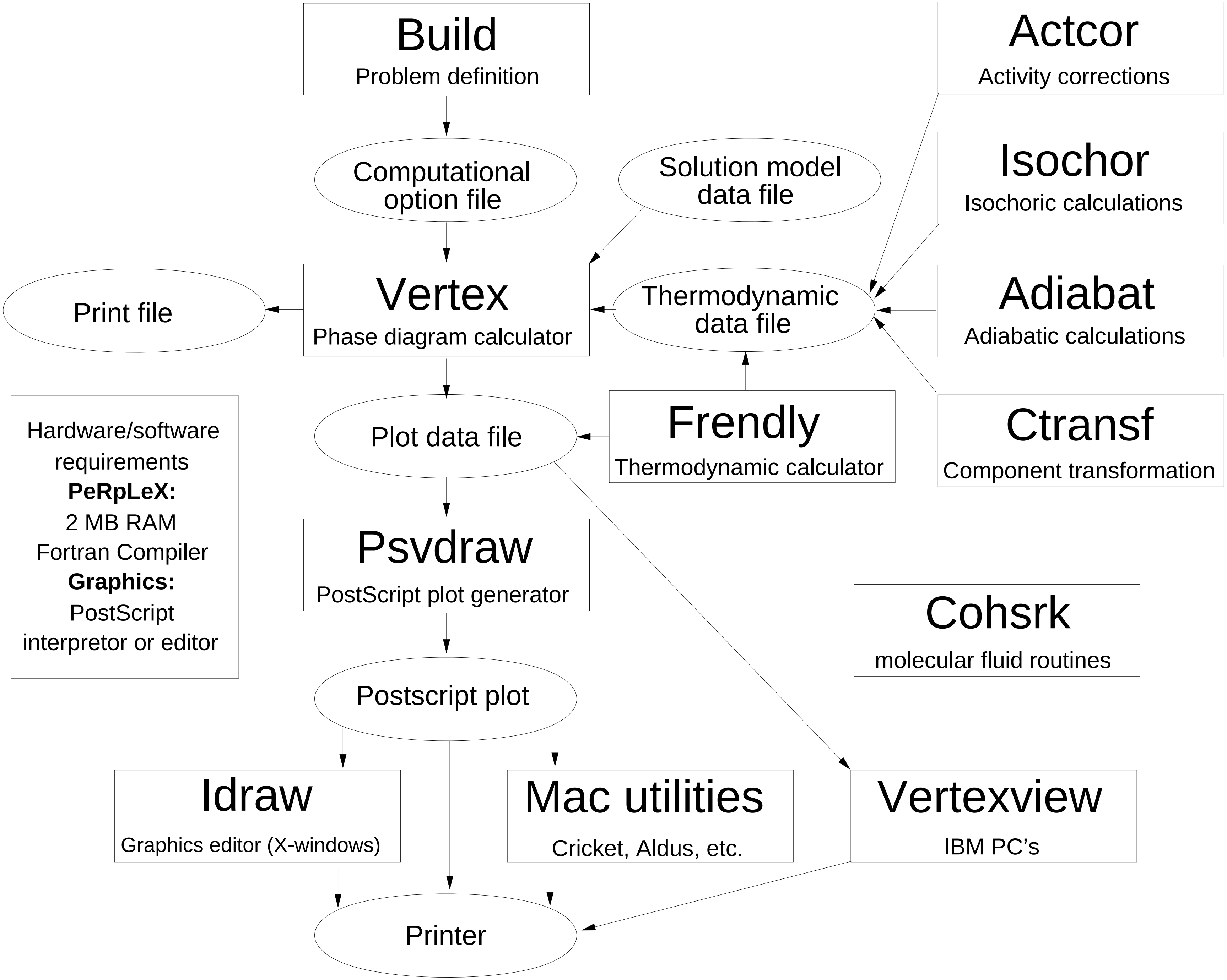


Fig 1.1 PeRpLeX program/file structure.

Figure 2.1

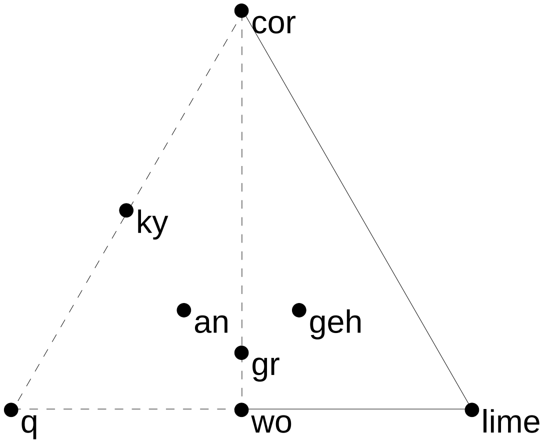


Figure 2.2

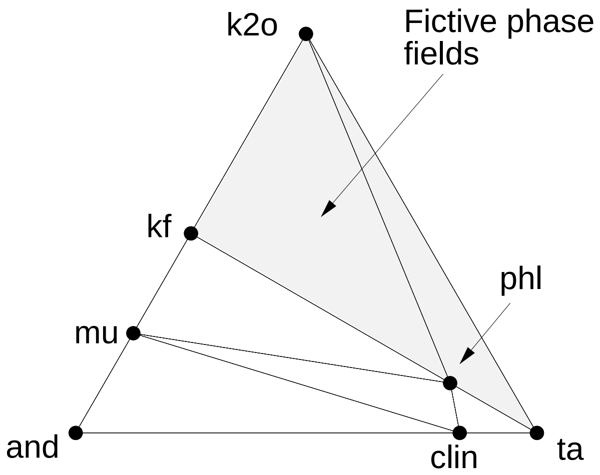


Figure 3.1

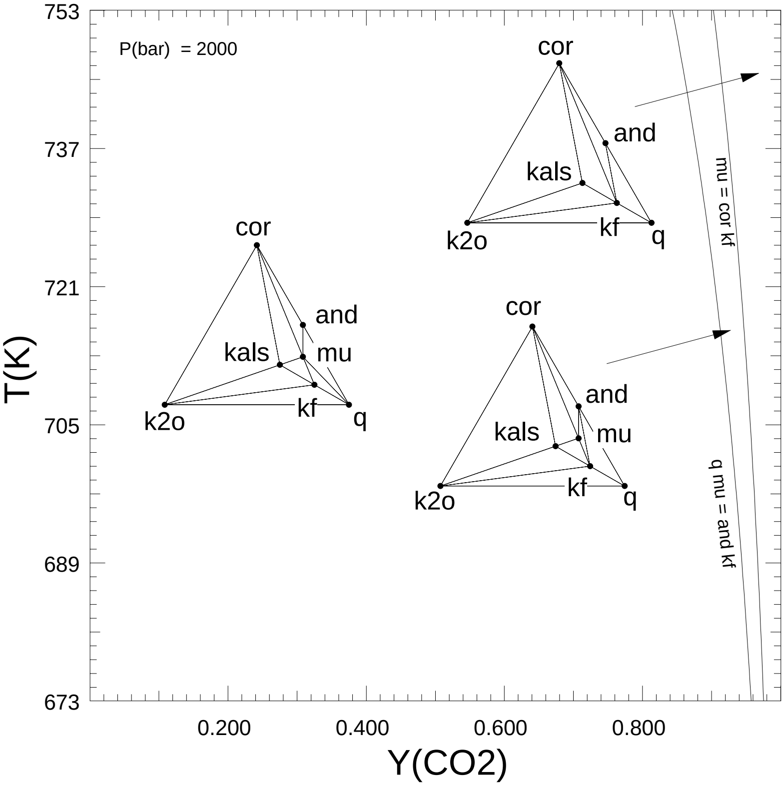


Figure 3.2

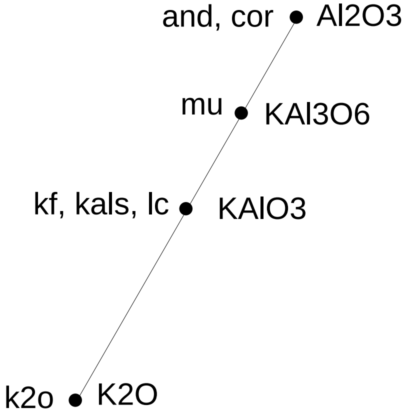


Figure 3.3

A Schreinemakers Projection (CaO-MgO)

Component saturation heirarchy: SIO2 KALO3 AL2O3

Reaction equations are written such that the high T(K)
assemblage is on the right of the = sign

P(bar) =0.200E+04

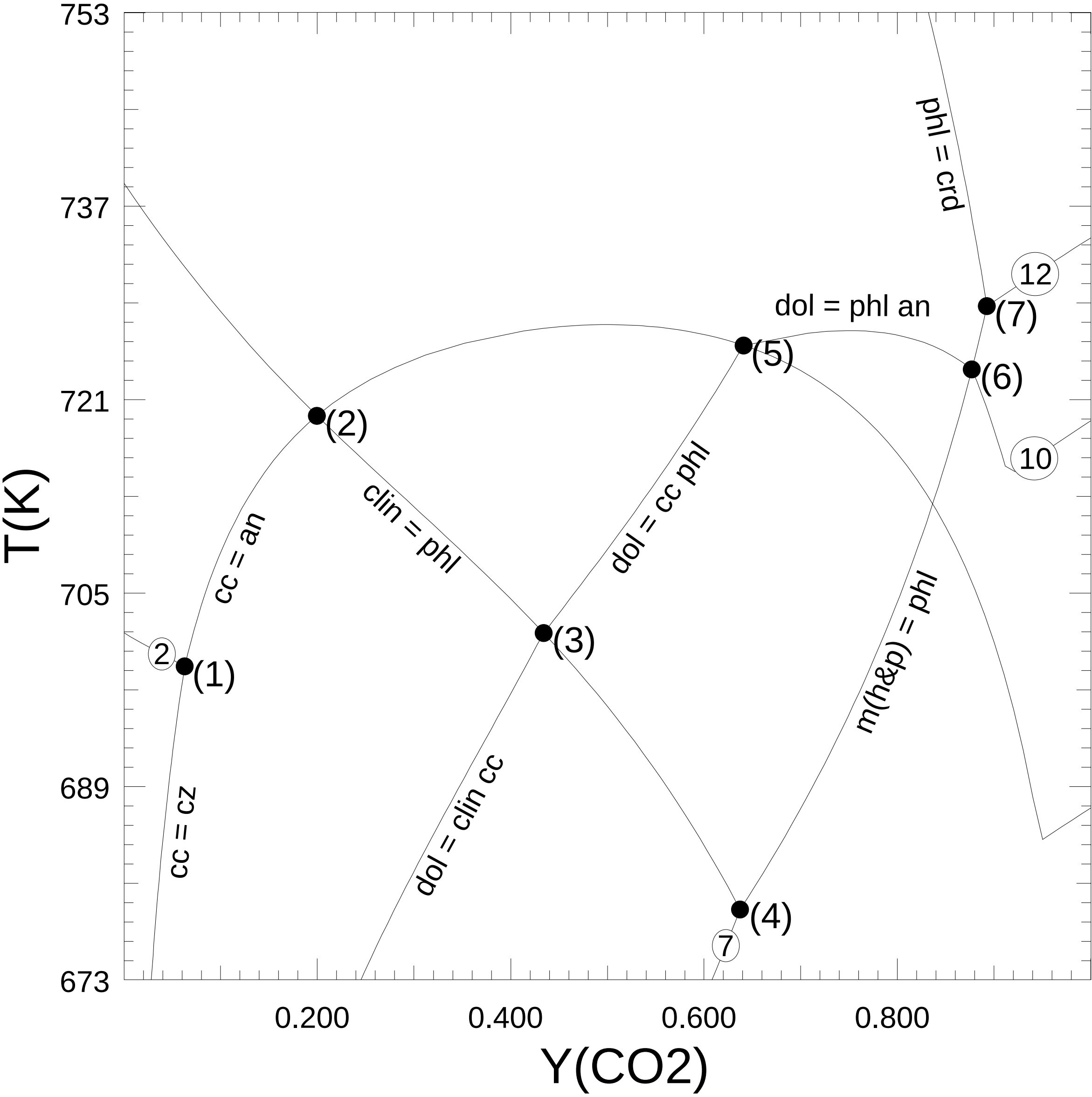
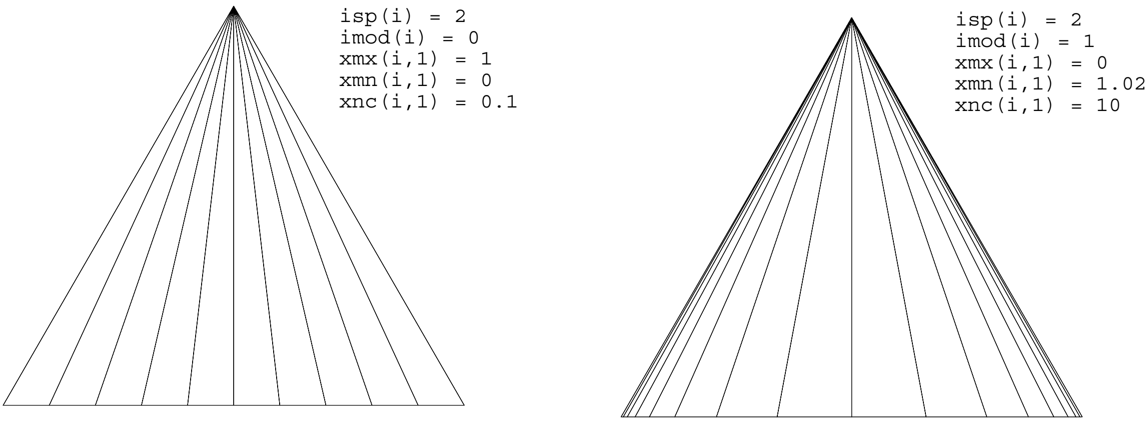


Figure 4.1. Pseudocompound subdivision schemes.

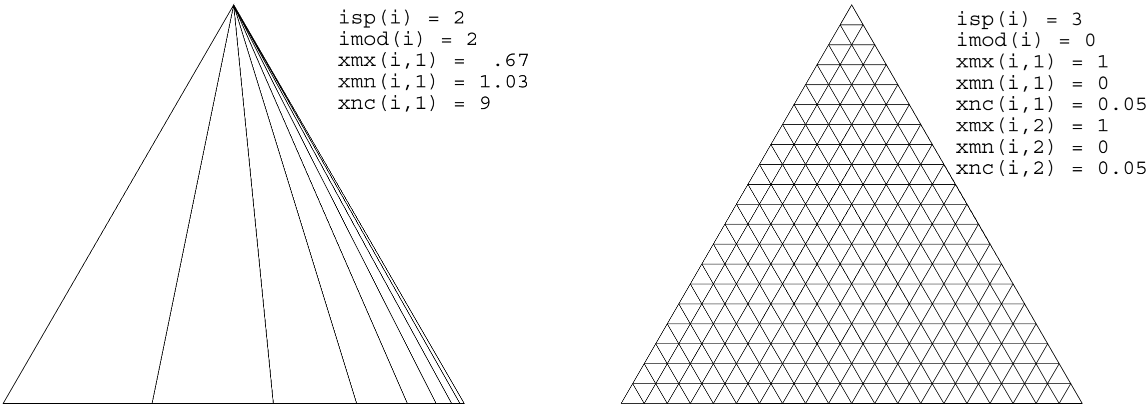


a) Cartesian binary.

isp(i) = 2
imod(i) = 0
xmx(i,1) = 1
xmn(i,1) = 0
xnc(i,1) = 0.1

b) Symmetric transform binary.

isp(i) = 2
imod(i) = 1
xmx(i,1) = 0
xmn(i,1) = 1.02
xnc(i,1) = 10

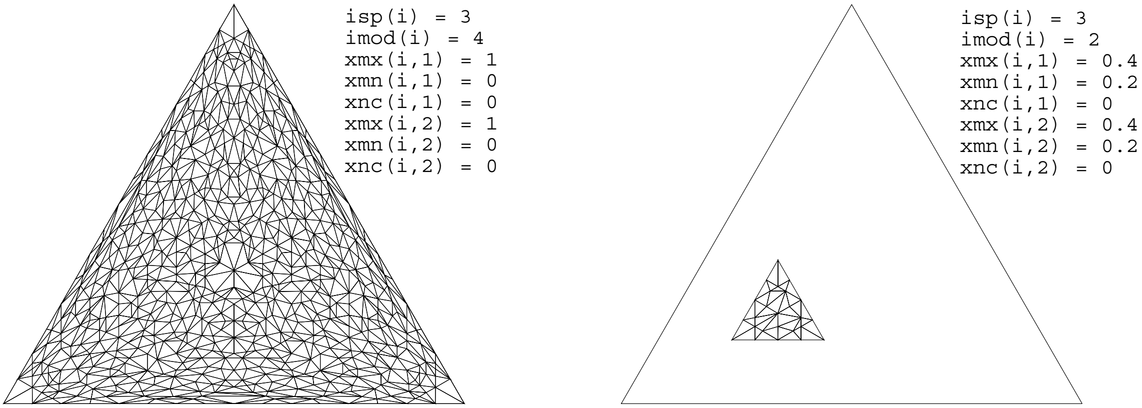


c) Asymetric transform binary.

isp(i) = 2
imod(i) = 2
xmx(i,1) = .67
xmn(i,1) = 1.03
xnc(i,1) = 9

d) Cartesian ternary.

isp(i) = 3
imod(i) = 0
xmx(i,1) = 1
xmn(i,1) = 0
xnc(i,1) = 0.05
xmx(i,2) = 1
xmn(i,2) = 0
xnc(i,2) = 0.05



e) Fourth order barycentric ternary.

isp(i) = 3
imod(i) = 4
xmx(i,1) = 1
xmn(i,1) = 0
xnc(i,1) = 0
xmx(i,2) = 1
xmn(i,2) = 0
xnc(i,2) = 0

f) Second order barycentric ternary.

isp(i) = 3
imod(i) = 2
xmx(i,1) = 0.4
xmn(i,1) = 0.2
xnc(i,1) = 0
xmx(i,2) = 0.4
xmn(i,2) = 0.2
xnc(i,2) = 0

Figure 4.2. An AFM diagram calculated with pseudocompounds.

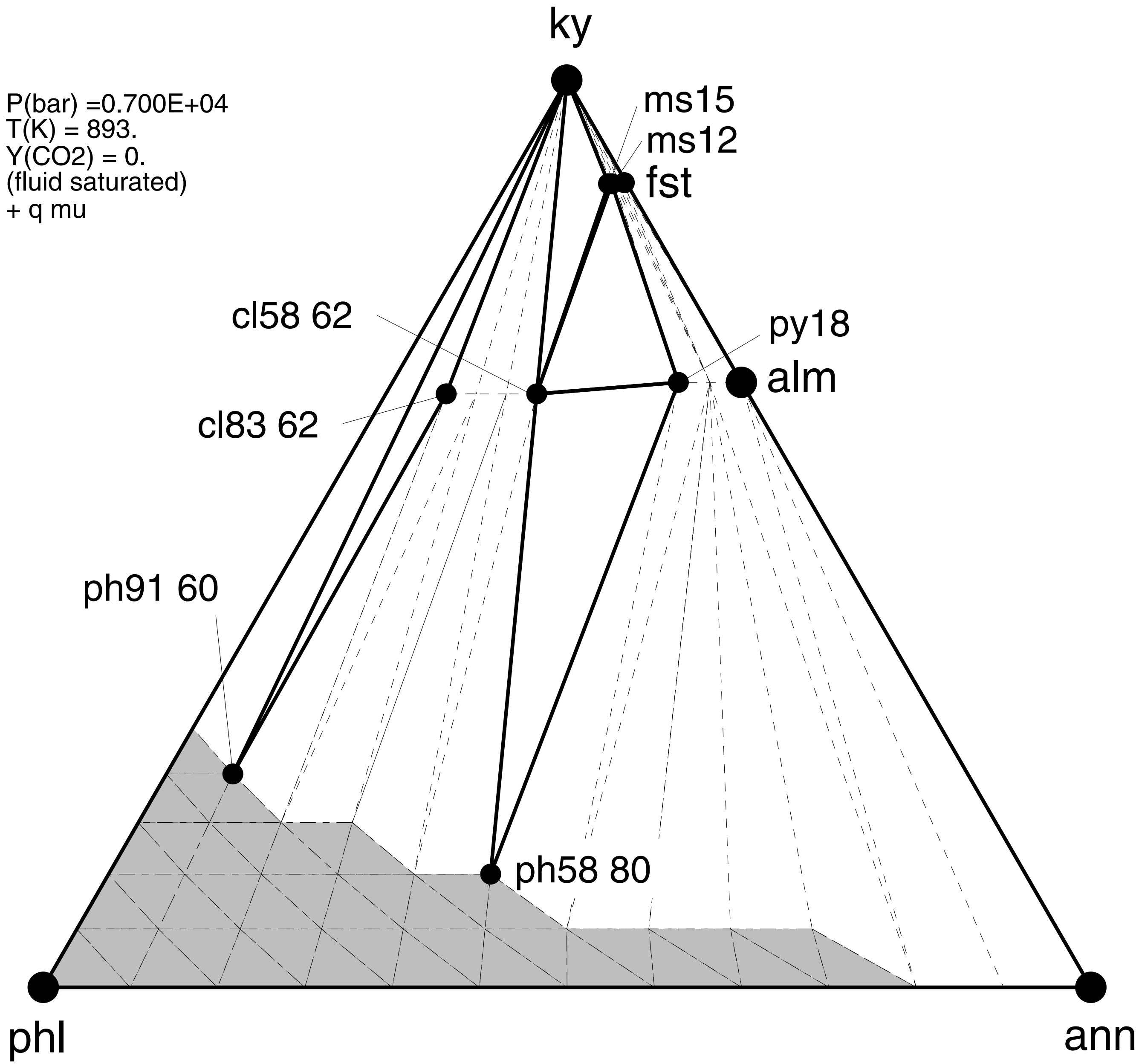
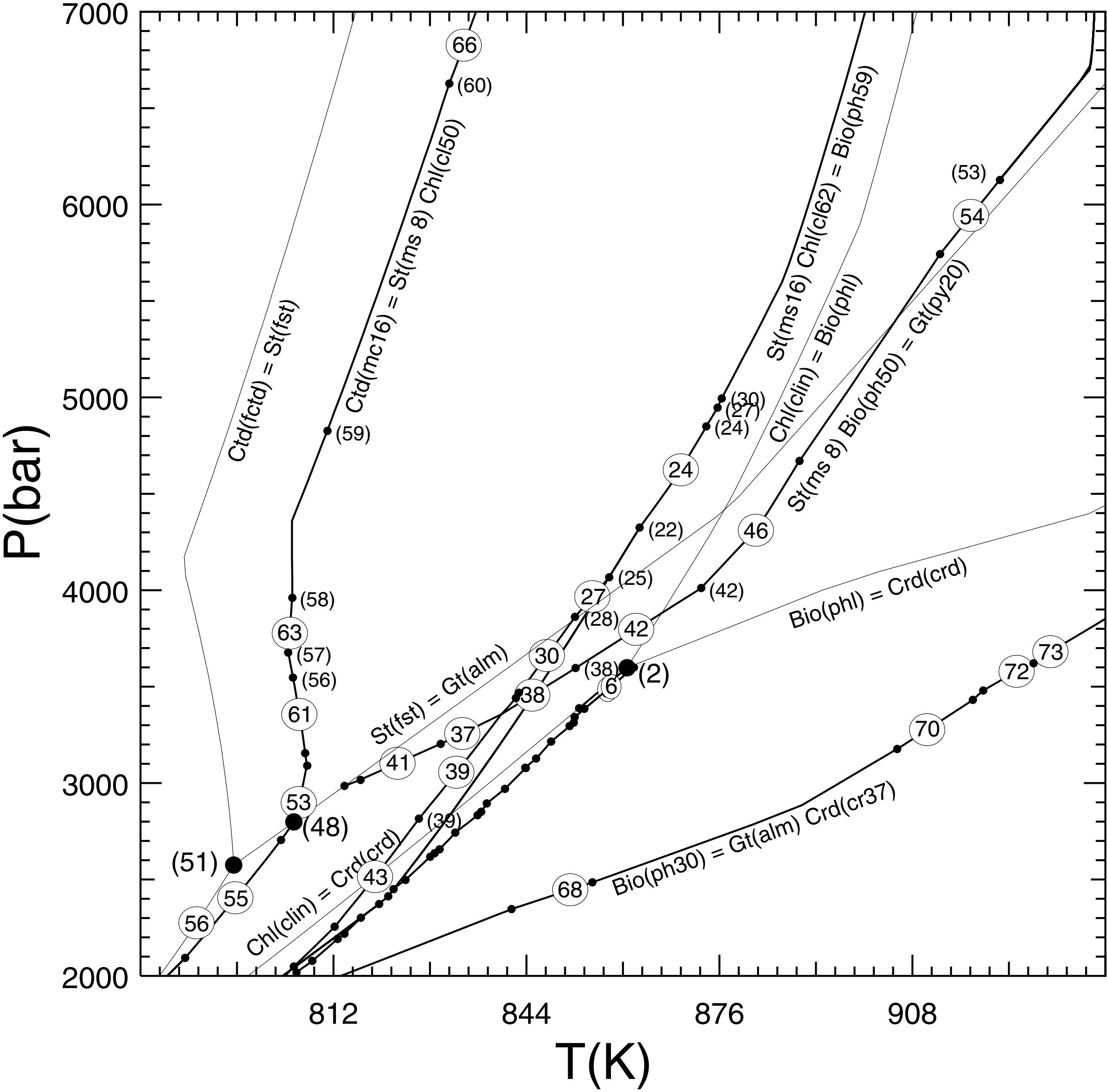


Figure 4.3


P(bar)
T(K)
7000
6000
5000
4000
3000
2000
812
844
876
908
Ctd(fctd) = St(fst)
Ctd(mc16) = St(ms 8) Chl(cl50)
St(ms16) Chl(cl62) = Bio(ph59)
Chl(clin) = Bio(phl)
St(ms 8) Bio(ph50) = Gt(py20)
Bio(phl) = Crd(crd)
St(fst) = Gt(alm)
Chl(clin) = Crd(crd)
Bio(ph30) = Gt(alm) Crd(cr37)
66
(60)
(59)
(58)
63
(57)
(56)
61
53
(48)
(51)
55
56
(53)
54
(30)
(27)
(24)
24
(22)
46
(25)
27
(42)
(28)
42
30
(38)
(2)
6
38
37
41
39
(39)
43
68
70
72
73

plop

Component saturation heirarchy: SIO2 AL2O3 K2O

Reaction equations are written such that the high T(K)
assemblage is on the right of the = sign

Y(CO2) = 0.

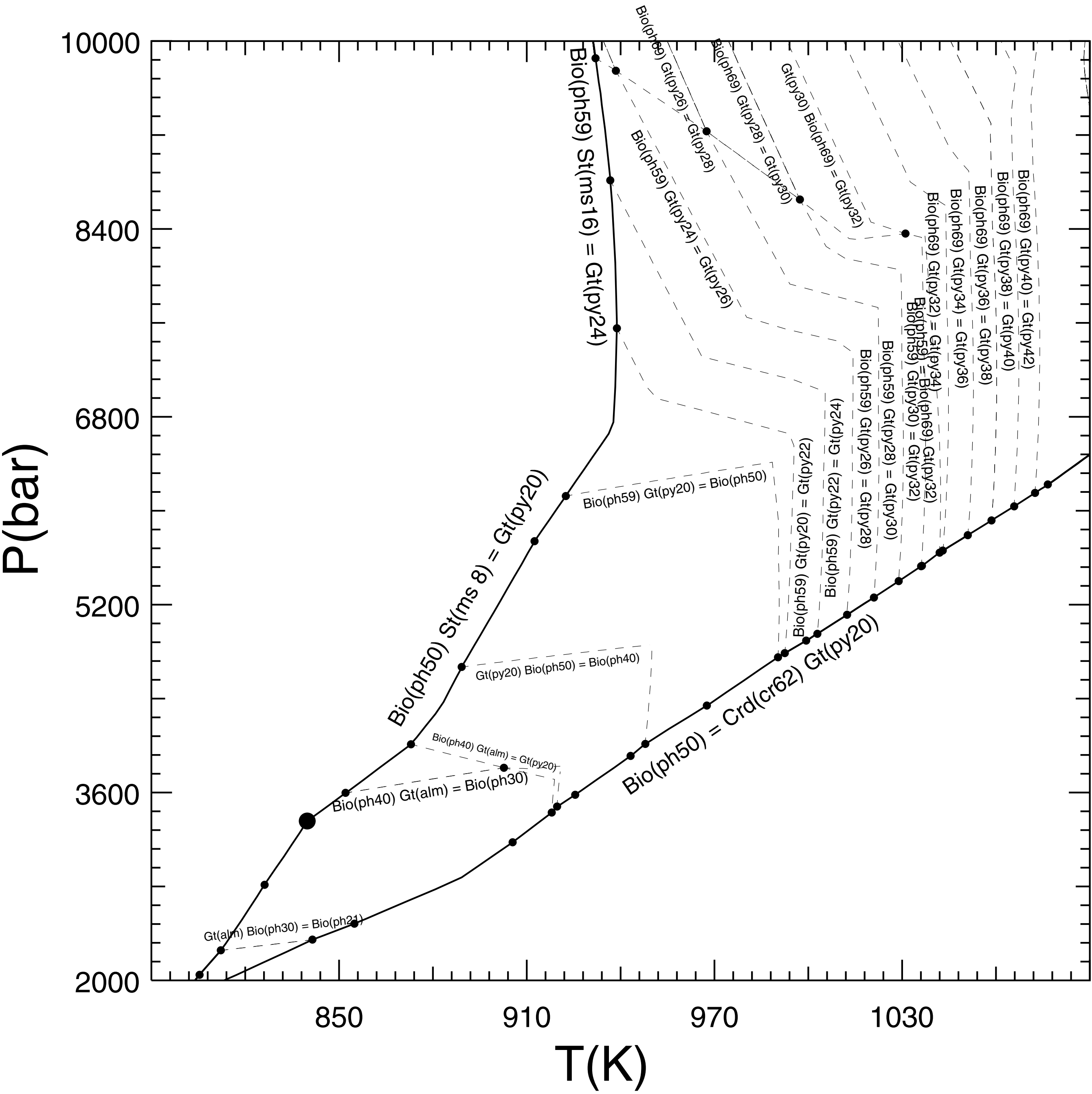


Fig 5.1. Mixed variable diagram for the FMASH system at 7 kbar after projection through quartz, aluminosilicate and muscovite. Calculated using data from files hp90ver.dat and solut.dat, the computational option file in51. Upper diagram as output by Psvdraw, lower after spline smoothing.

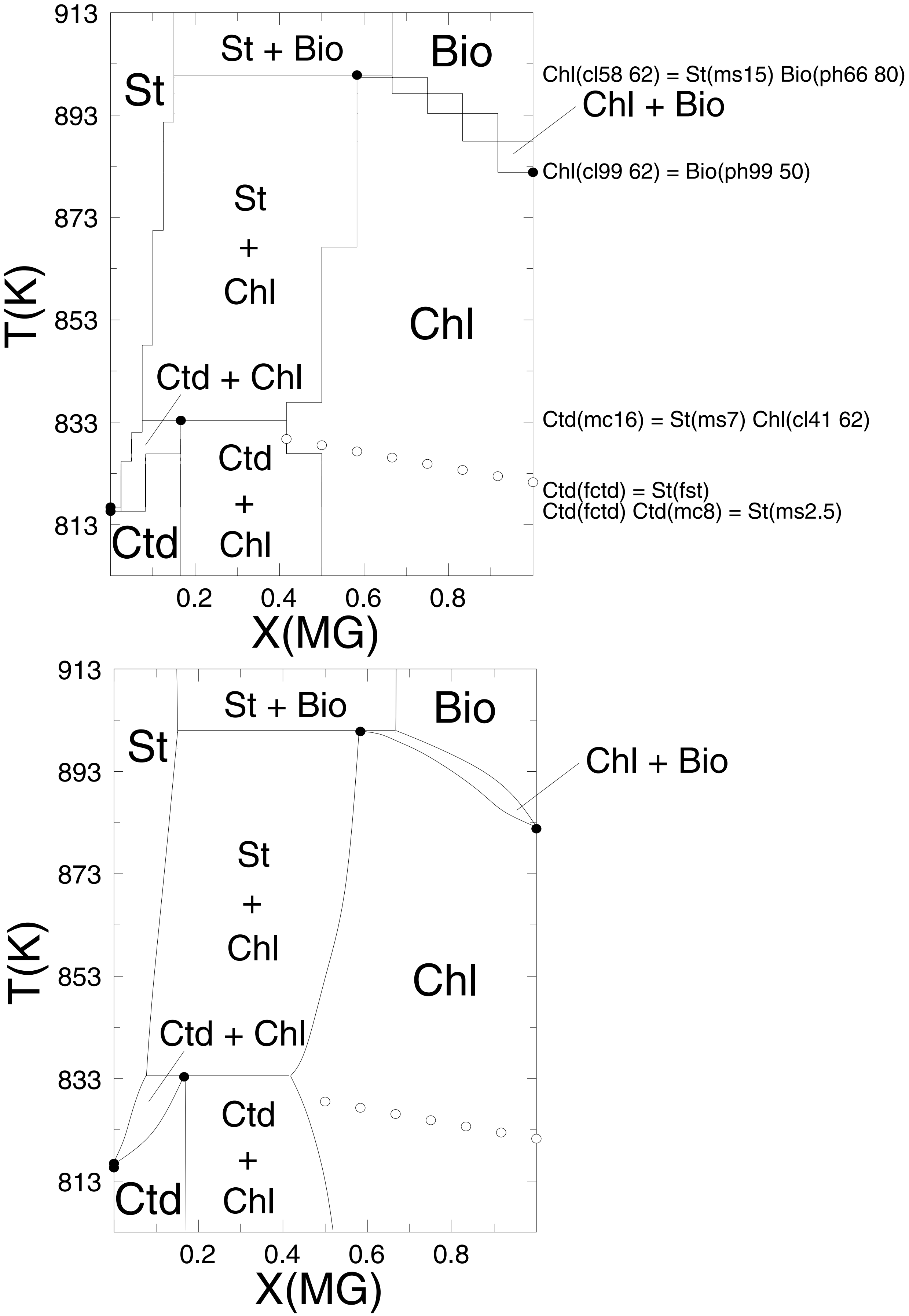
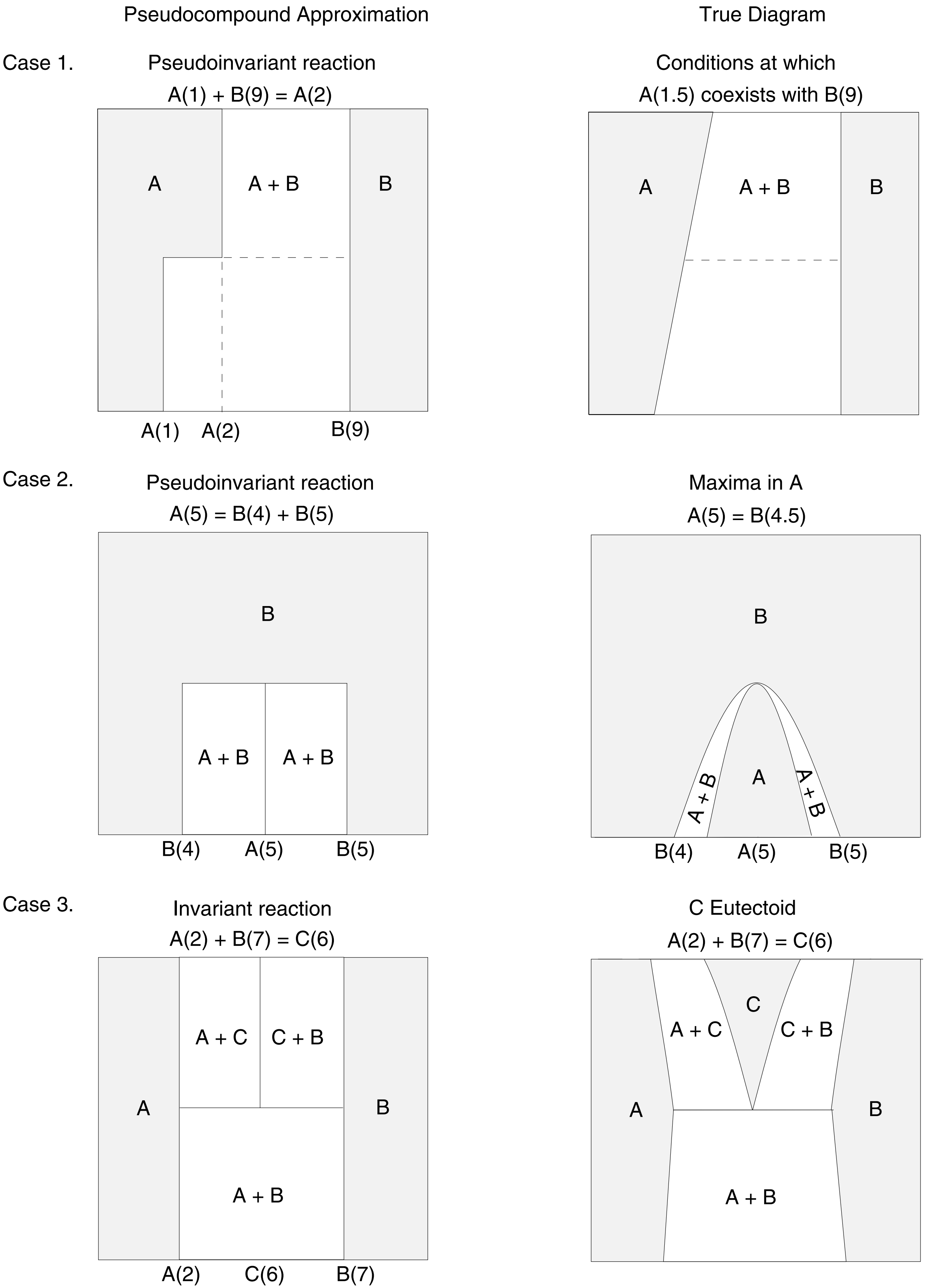


Fig 5.2. Relation between pseudocompound relations and real phase diagram features. Schematic pseudocompounds are given sequential numbering, e.g., the average composition of compounds A(1) and A(2) is A(1.5).



Pseudocompound Approximation

True Diagram

Case 1. Pseudoinvariant reaction A(1) + B(9) = A(2)

Conditions at which A(1.5) coexists with B(9)

Case 2. Pseudoinvariant reaction A(5) = B(4) + B(5)

Maxima in A A(5) = B(4.5)

Case 3. Invariant reaction A(2) + B(7) = C(6)

C Eutectoid A(2) + B(7) = C(6)

Fig 5.3

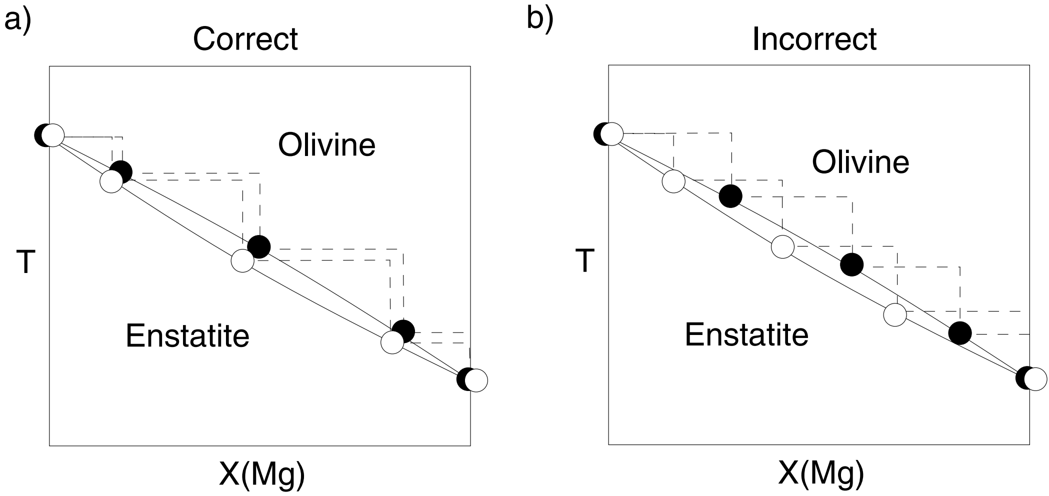


Fig 5.4

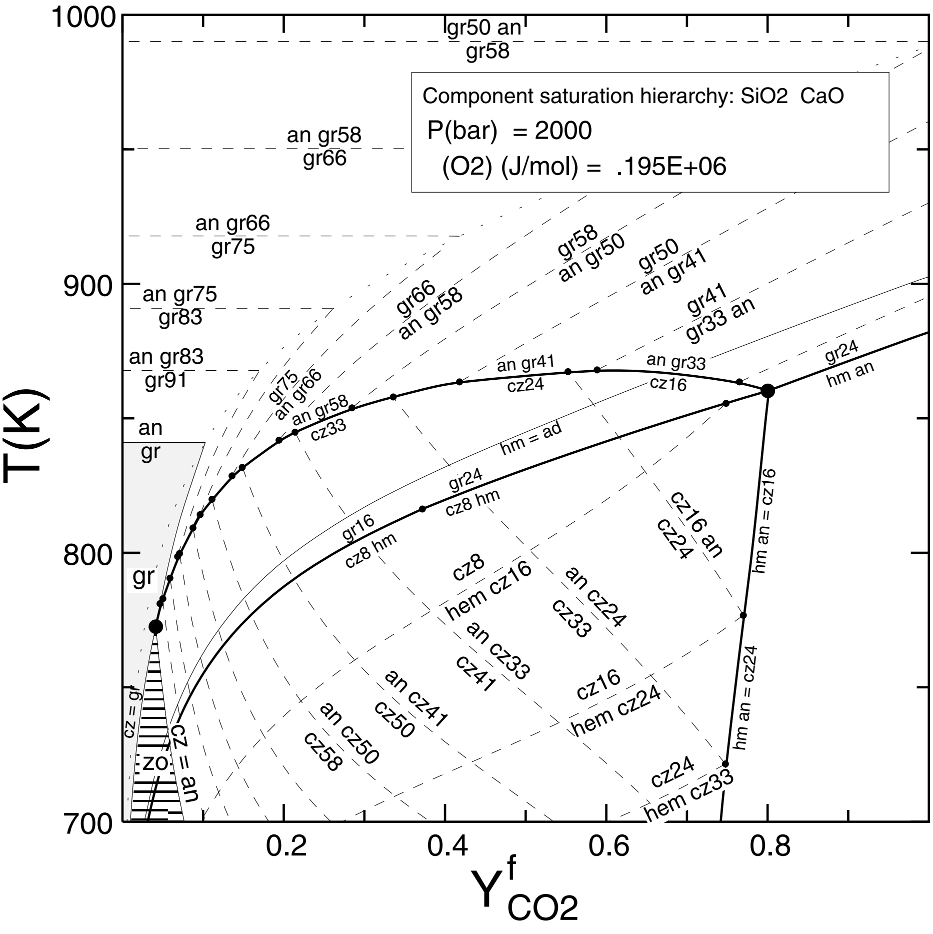


Fig 5.5

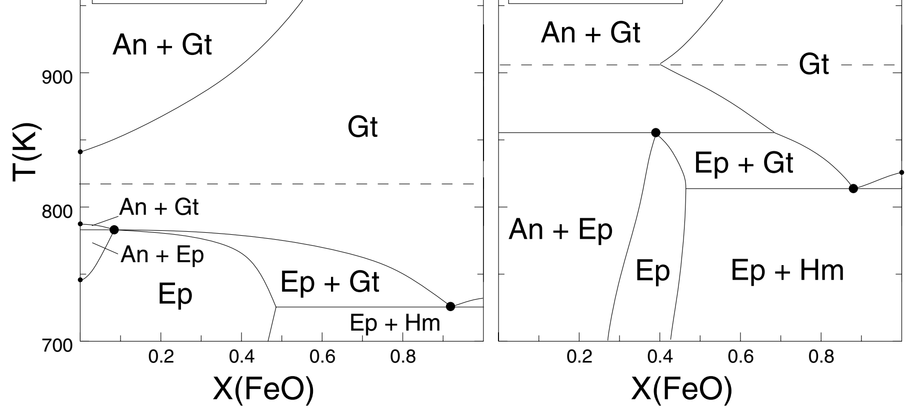
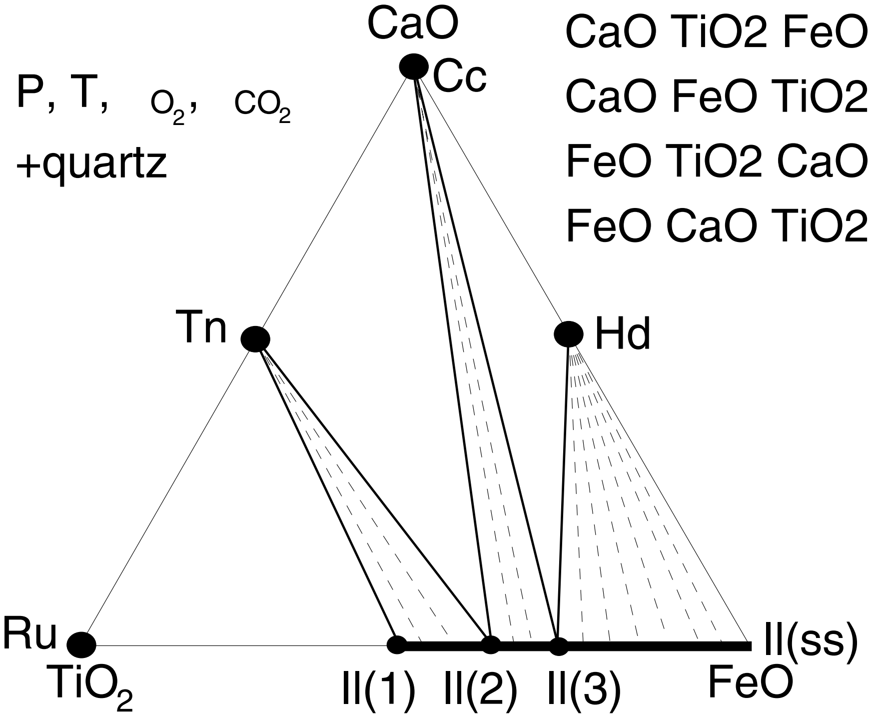
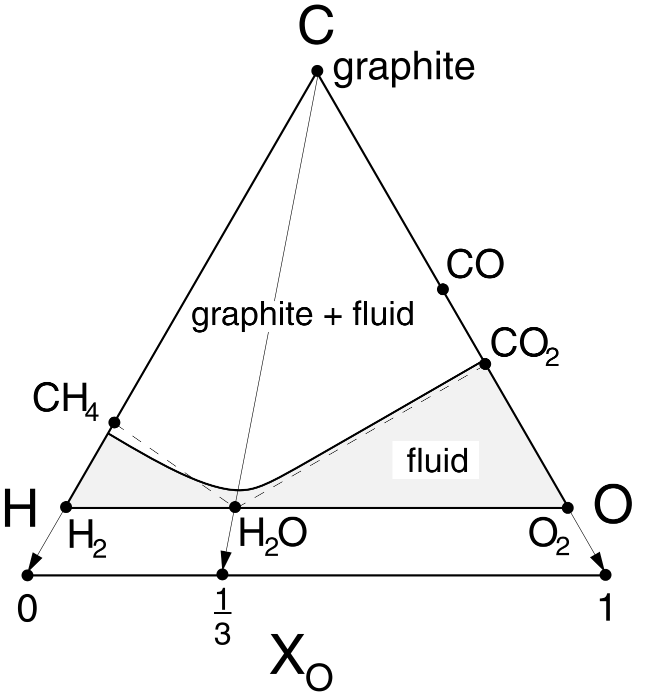


Fig 5.6 Valid component saturation hierarchies after projection through SiO2, CO2, and O2 in the system CaO TiO2 FeO, The saturated phases are indicated for each hierarchy, assuming the phase compatibilities shown in the composition diagram.

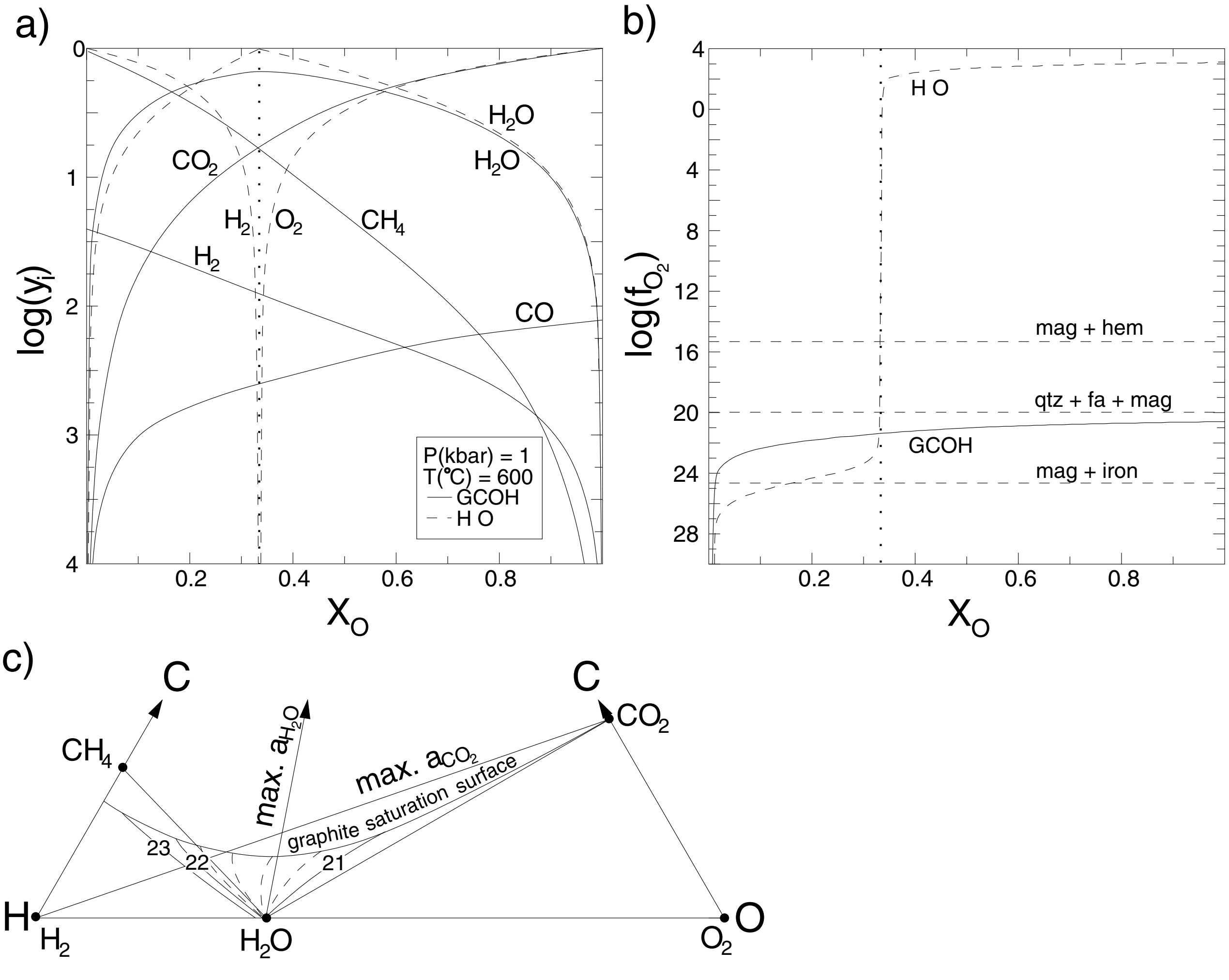
Hierarchy	Saturated Phases
TiO2 FeO CaO	Ru + Il(1) + Tn
TiO2 CaO FeO	Ru + Tn + Il(1)
CaO TiO2 FeO	Cc + Tn + Il(2)
CaO FeO TiO2	Cc + Hd + Il(3)
FeO TiO2 CaO	Invalid
FeO CaO TiO2	Invalid



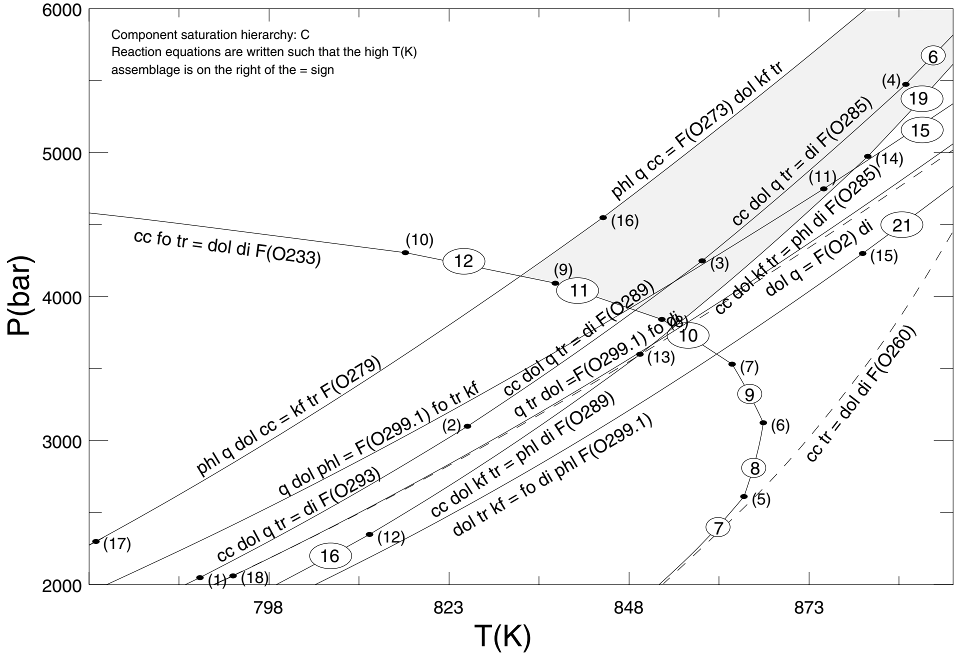
Tutorial Fig 6.1



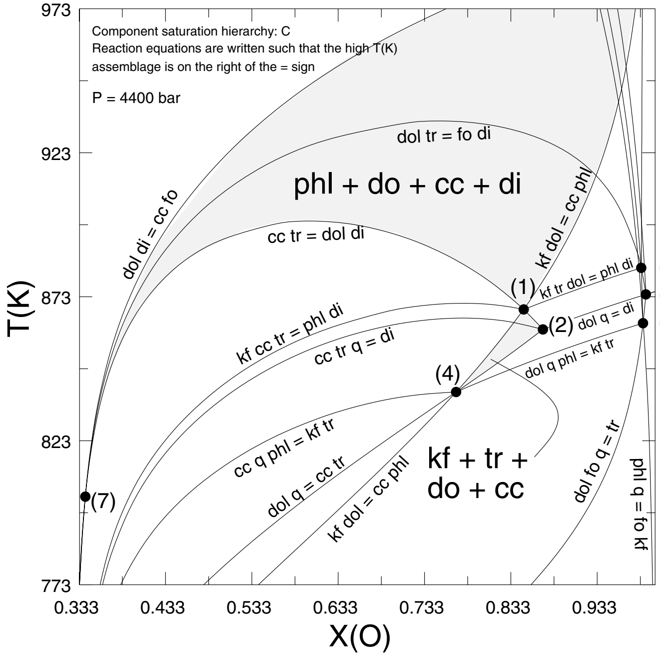
Tutorial Fig 6.2. Speciation (a) and f(O2) (b) of graphite saturated COH (GCOH, solid curves) and OH (dashed) fluids at 600 C and 1 kbar. (c) Contours of log(f(O2)) on the COH composition space at 600 C and 1 kbar (from Connolly 1994).



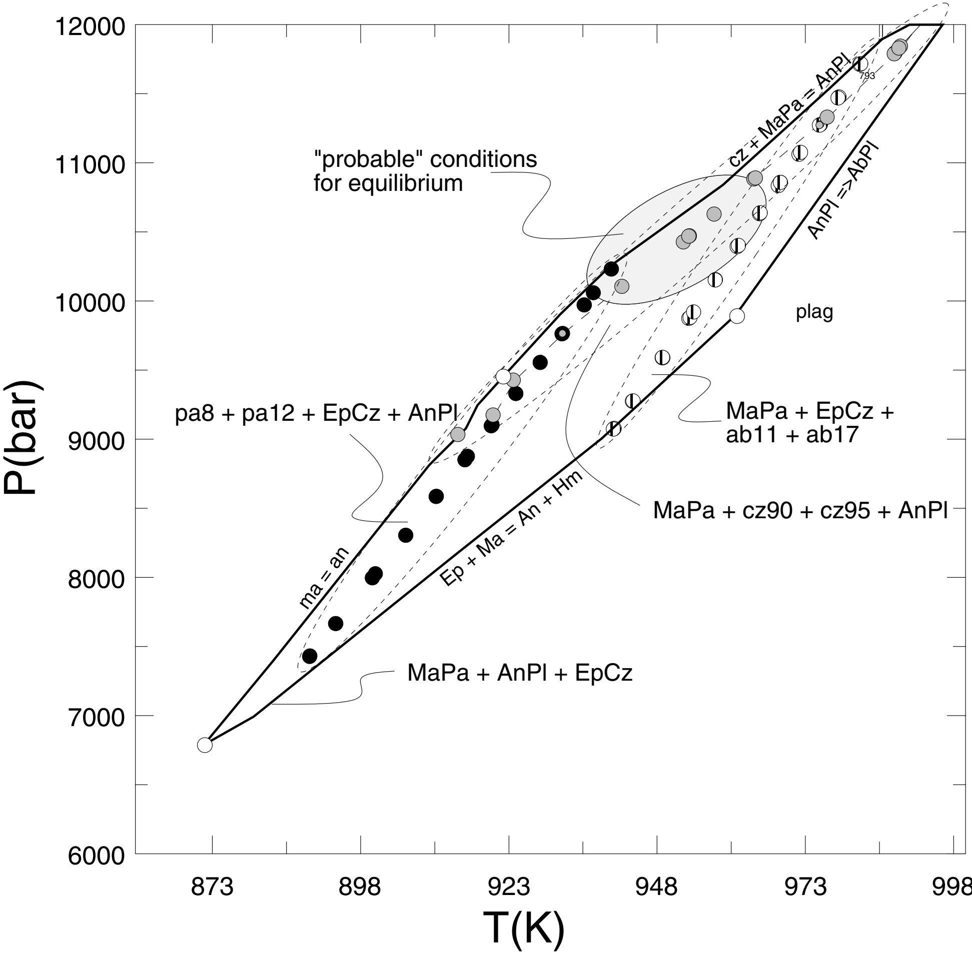
Tutorial Fig 7.1



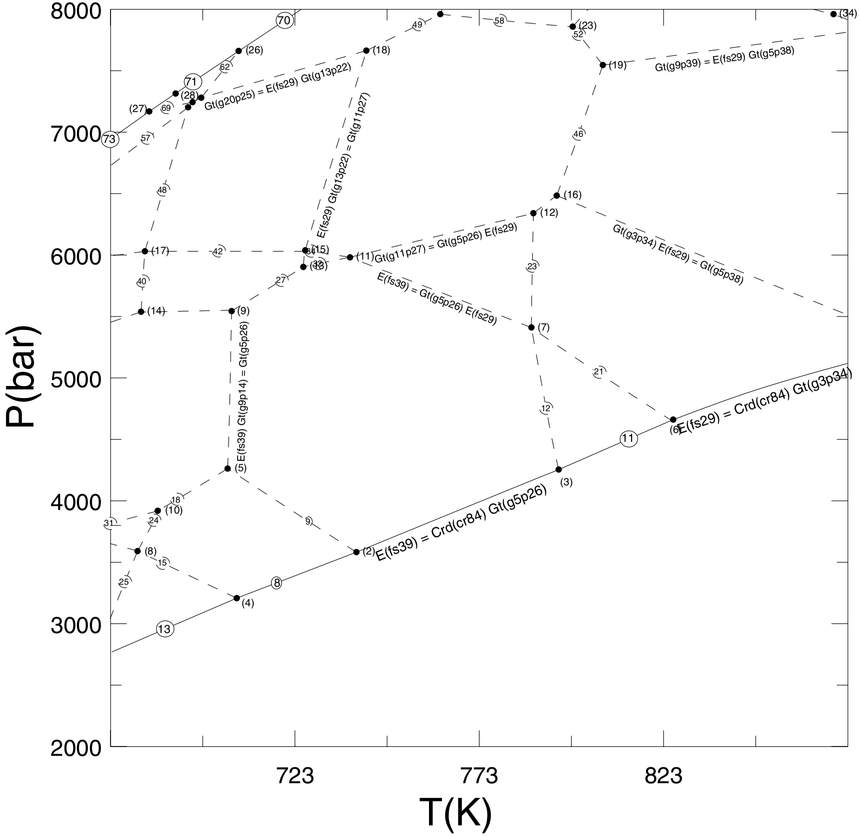
Tutorial Fig 7.2



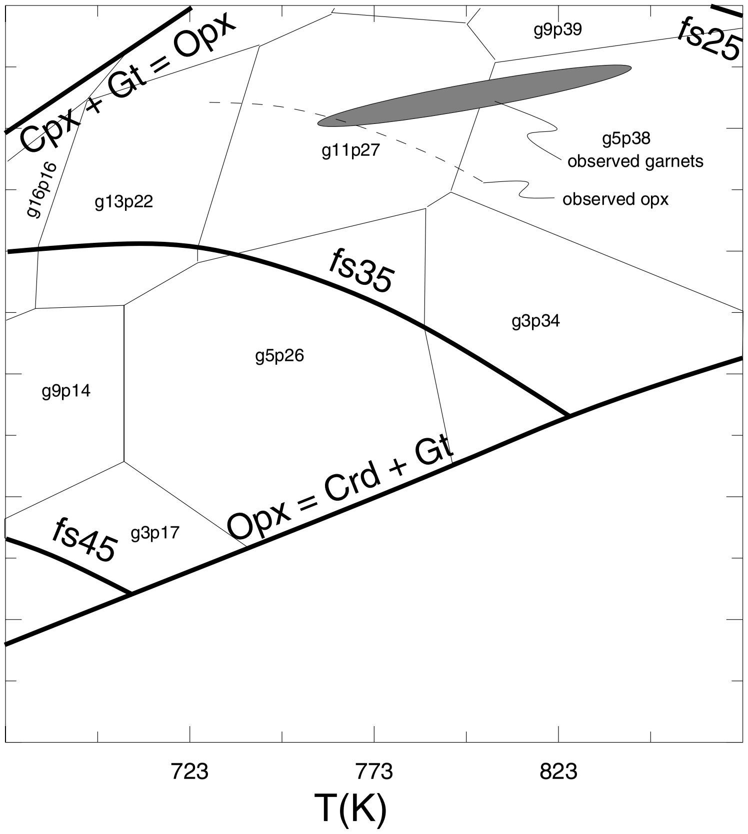
Tutorial Fig 8.1



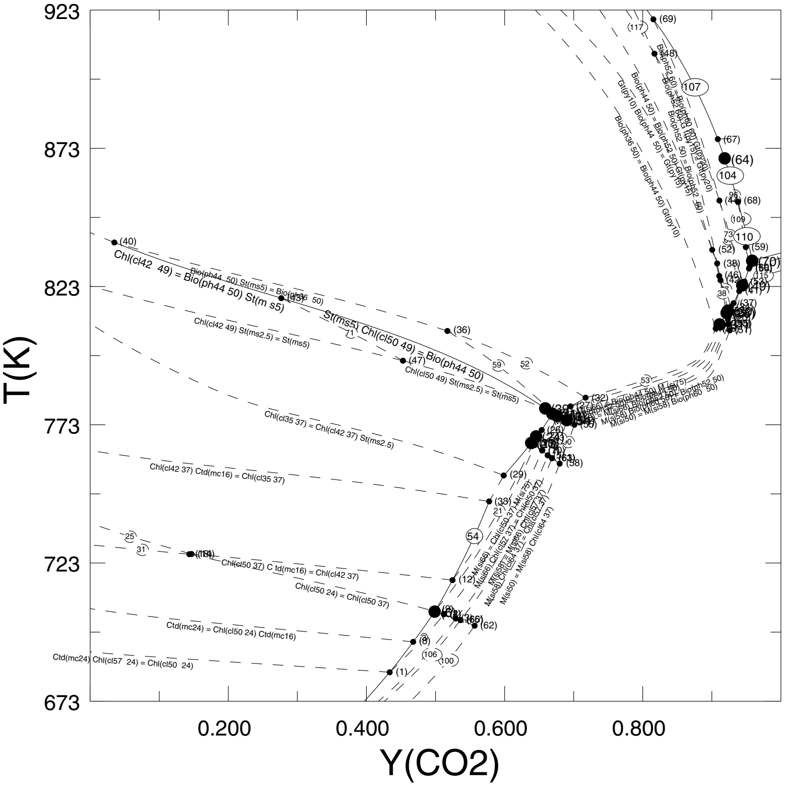
Tutorial Fig 8.2a



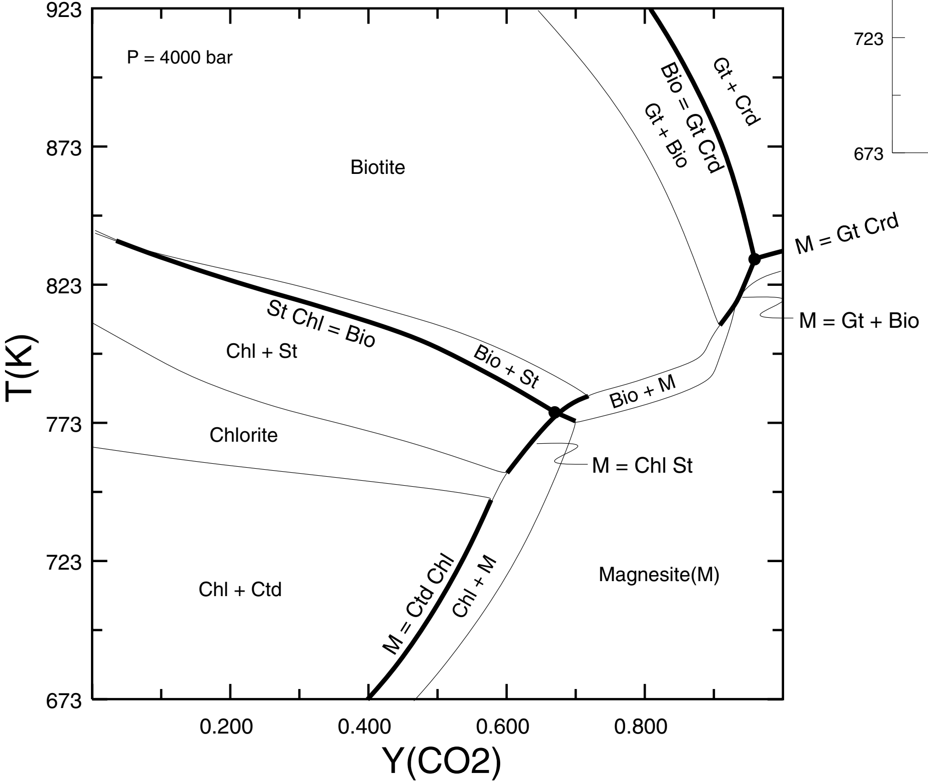
Tutorial Fig 8.2b



Tutorial 9.1a



Tutorial 9.1b



Tutorial 9.1c