Phase diagram introduction
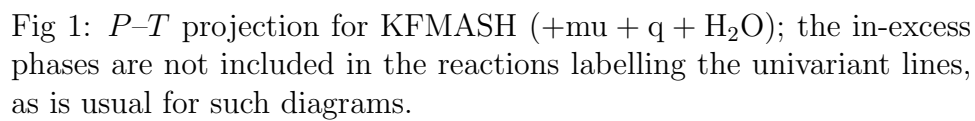
Much of the simple systematics of phase diagrams is covered in some unpublished course notes that RP built up over the years, reaching the form that they take below in 1991. They are reproduced in their entirety, starting

Some introductory material (based on Powell *et al.*, 1998) can be used to set the scene here: calculating phase diagrams involves a number of steps:

1. *Choose a model system in which to do the calculations.* A model system is just the chemical system, usually specified in terms of oxides, in which the equilibria to be calculated can be represented. This specifies which phases, and the substitutions within them, that will be able to be considered. Obviously these phases can only involve those end-members that occur in the thermodynamic dataset used (or linear combinations of them). For example, the model system normally used to consider metapelites is K_2O–FeO–MgO–Al_2O_3–SiO_2–H_2O (or KFMASH) (Thompson, 1957), allowing most of the critical minerals, and the $FeMg_{-1}$ and $(Fe,Mg)SiAl_{-1}Al_{-1}$ (Tschermak's) substitutions in them, to be considered. This model system is the one used for some examples below.

2. *Formulate the thermodynamics of the phases in the system.* Given that a central part of calculations on assemblages involving solid solutions is the calculation of the equilibrium compositions of the phases, the activity-composition (a–x) relationships of the phases are needed in algebraic form, in terms of the compositional variables to be calculated.

3. *Decide on which phase diagrams are to be constructed.* This decision will depend mainly on what geological problems are being addressed. Important types of diagrams are:

    - A *P–T projection*, usually a key phase diagram, shows the stable invariant points and univariant (or reaction) lines for all of the bulk compositions in the system. A *P–T* projection for KFMASH, constrained by stipulating the presence of muscovite, quartz and H_2O (i.e. with mu + q + H_2O "in excess"), is shown in Fig. 1. Such diagrams are the familar petrogenetic grids of the literature.

    - *Compatibility diagrams* show the mineral assemblages, and ranges of mineral solid solutions, at specified *P–T*, for all of the bulk compositions in the model system. A compatibility diagram for AFM, with mu + q + H_2O in excess, is shown in Fig. 2.

    - *P–T pseudosections* show just those phase relationships for a particular bulk composition. A *P–T* pseudosection for a model pelite composition in AFM, with mu + q + H_2O in excess, is shown in Fig. 3.

    - *T–x* or *P–x pseudosections* show the phase relationships for a particular bulk composition line, at specified *P* or *T* respectively. A *T–x* pseudosection for AFM, with mu + q + H_2O in excess, is shown in Fig. 4.

Fig 1

AFM
(+ mu + q + H$_2$O)

Pressure (kbar) — 14, 12, 10, 8, 6, 4, 2, 0

Temperature (°C) — 450, 500, 550, 600, 650, 700

[bi cd chl]
als g / cd st
ctd / g chl als
[bi cd]
chl g / bi als
g als / st chl
[ctd cd]
g als / st bi
ky / sill
ctd ky / chl st
ctd / g chl st
g chl / st bi
st chl / bi als
g chl / ctd bi
[cd als st]
[ctd g st]
[cd als]
ky / and
chl ctd / st bi
[cd als chl]
chl als / cd bi
st bi / g als
sill / and
ctd chl / bi als
[g cd]
[ctd cd chl]
als chl / ctd cd
[g st]
ctd als / st bi
ctd chl / cd bi
[g st chl]
[g cd chl]

Fig 1: *P–T* projection for KFMASH (+mu + q + H$_2$O); the in-excess phases are not included in the reactions labelling the univariant lines, as is usual for such diagrams.

Fig 2

AFM
(+ mu + q + H$_2$O)

6.0 kbar
560°C

ky
st
g
chl
bi

Fig 2: AFM compatibility diagram for KFMASH (+mu + q + H$_2$O) at *P* = 6 kbar and *T* = 560°C
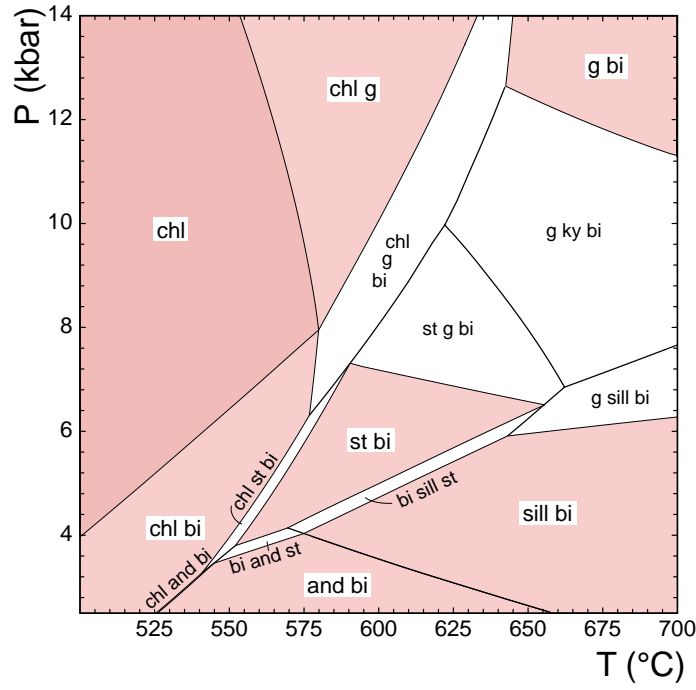
Fig 3: P–T pseudosection in KFMASH (+mu+q+H_2O) for a "common" pelite composition: $Al_2O_3 = 41.89$, $MgO = 18.19$, $FeO = 27.29$, and $K_2O = 12.63$ (in mol%)
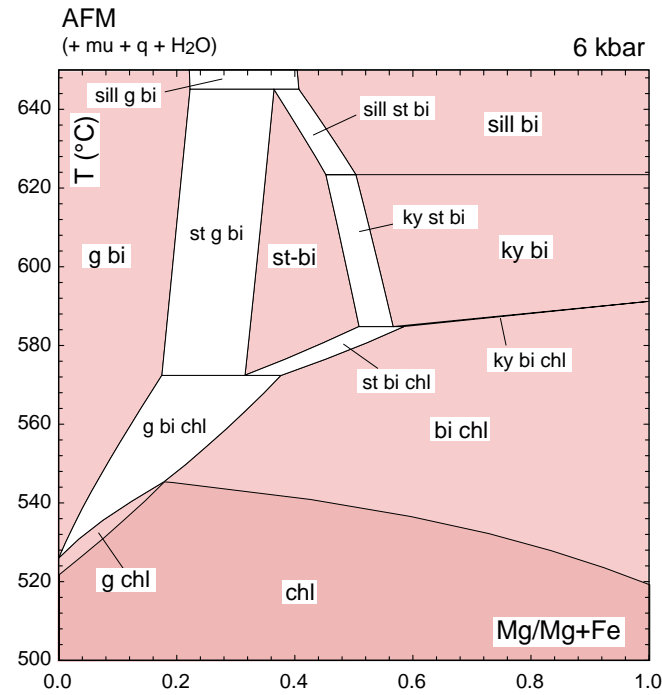

Fig 4: A T–x pseudosection in KFMASH (+mu+q+H_2O), for a composition line along which FeO:MgO varies, with $x = FeO/(FeO+MgO)$, and $Al_2O_3 = 41.89$, Fe0 + MgO = 45.48, and $K_2O = 12.63$ (in mol%). This composition line goes through the composition used in Fig. 3.

Pseudosections are important because in systems with solid solutions, it is not usually obvious which parts of the equilibria in a P–T projection will be seen by a particular bulk composition, given that the compositions of the phases vary along the univariant lines (compare Figs 3–4 and Fig. 1).

The diagrams in Figs 1–4 were of course calculated with the program THERMOCALC. Although there are other types of phase diagrams that can be drawn, for example with activities or chemical potentials on the axes, the calculation of the types of diagram in Figs 1–4 will be the focus of the workshop.

4. *Build up the phase diagram via calculations on the equilibria involved.* Each mineral equilibrium calculation involves setting up and solving a mathematical problem, that, in THERMOCALC, involves solving a set of non-linear equations. Generating a phase diagram usually involves many such calculations. Phase diagrams can be drawn from THERMOCALC output using the new software, DRAWPD.

Metamorphic phase diagrams: Course Notes 2000

These notes do not correspond directly—in content or in order—with what will be covered in the course. They provide, in different parts: something of a glossary, a summary of some ideas, technical background material, practical methods. I do not pretend that the notes are 'complete'! Think of them as necessary but not sufficient for your phase diagramming... (If you would like to quote these notes, refer to "Powell, R., 1991. *Metamorphic Mineral Equilibria Short Course*: Course Notes. University of Melbourne"). This is a minor revision (and TEX-ing) of those hand-written 1991 notes.

System is used in two ways (the meaning is usually obvious by context):

1. for a *range* of chemical compositions eg all possible compositions in $KAlO_2$-FeO-MgO-Al_2O_3-SiO_2-H_2O (KFMASH), or at least all possible compositions attainable with the phases chosen to be considered. This example system is a model for many pelites but also includes many compositions unlike any rocks. The term sub-system is used for a part of a system, so KMASH is a sub-system of KFMASH.

2. for an example composition in a range of chemical compositions. So, system, used in this way, may correspond to a rock, including any fluid on grain boundaries during metamorphism. The composition of such a system can be referred to as the system composition or, more commonly, the *bulk composition* of the system. If the context is an equilibrium one, the system is that part of the rock which is in equilibrium. This may well exclude the cores of porphyroblasts for example. This sort of system corresponds to the idea of an *equilibration volume* .

A system, as an example composition, can be described in terms of:

- the proportions of phases (proportions of minerals, fluids, silicate liquids)—as in the mode of a rock.

- the proportions of components. Components come in independent sets, a set of independent components involving the *minimum* number of chemical compounds of fixed composition which can be used to describe all the chemical variations in a system. In many systems a set of oxides makes an independent set. There are always many possible independent sets. The choice of the set is usually made on the basis of diagrammatical convenience. Of course, for a particular system, any independent set can be expressed in terms of any other independent set. For example, the pelite system, K_2O-FeO-MgO-Al_2O_3-SiO_2-H_2O is often considered in terms of $KAlO_2$-FeO-MgO-Al_2O_3-SiO_2-H_2O, with $KAlO_2$ instead of K_2O. But, to look at andalusite-sillimanite-kyanite stabilty, this is a one component system involving Al_2SiO_5 in Al-Si-O. There is no problem in having negative proportions of components.

Equilibrium in a system is defined thermodynamically by the equality of the chemical potentials of every component in every phase. Practically there is therefore a problem with using this definition because minerals have a stoichiometry—a fixed relationship between sites—making it difficult to arbitrarily add components, say SiO_2 to pyroxene, keeping FeO, MgO etc fixed. Such additions *are* possible, albeit in infinitesmal amounts, via defects, so there is no problem with the definition. Operationally, however we proceed using *end-members* of phases.
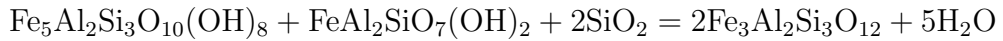
End-members of a phase are chemical compounds of fixed composition which have the stoichiometry of the phase into which they substitute, for example $CaMgSi_2O_6$ in clinopyroxene. In general, each phase has different end-members. There is no operational difficulty with respect to defining the chemical potential of an end-member of a phase because any end-member can be added to or subtracted from a phase holding the amount of the other end-members constant. It is straightforward to show that, for example, in a clinopyroxene:

$$\mu_{CaMgSi_2O_6} = \mu_{CaO} + \mu_{MgO} + 2\mu_{SiO_2}$$

This amounts to a statement of *internal equilibrium* in the phase. We can now restate the equilibrium definition—the chemical potentials of each component are equal in every phase—in terms of end-members of phases by saying that for each reaction between end-members of phases, that that reaction written in terms of chemical potentials is an equilibrium relationship; or:

$$\Delta\mu = 0$$

where Δ is an operator, with Δa meaning $\sum r_i a_i$, with r_i a reaction coefficient. For example, for a reaction between the end-members of the phases for equilibrium between garnet, chlorite, chloritoid, quartz and H_2O:

$$Fe_5Al_2Si_3O_{10}(OH)_8 + FeAl_2SiO_7(OH)_2 + 2SiO_2 = 2Fe_3Al_2Si_3O_{12} + 5H_2O$$

gives an equilibrium relationship for this assemblage:

$$\mu_{Fe_5Al_2Si_3O10(OH)_8} + \mu_{FeAl_2SiO7(OH)_2} + 2\mu_{SiO_2} = 2\mu_{Fe_3Al_2Si_3O_{12}} + 5\mu_{H_2O}$$

In this, for example $r_{SiO_2} = -2$ and $r_{H_2O} = 5$.

Model system , by which is meant a well-defined system, for example $KAlO_2$-FeO-MgO-Al_2O_3-SiO_2-H_2O for pelites, rather than a real system, corresponding to real rocks. The problem with real systems is that they include a spectrum of elements, from major, through minor, to trace, and it is difficult to say at which level an element no longer contributes to the phase equilibria. The approach is to study in detail a model system which 'models' real rocks, but to have a good idea how excluded elements might perturb the results.

Phase diagrams summarise phase equilibria for model systems. How phase diagrams may be applied to a rock depends on how well the model system approaches the real system, and how well the mineral textures and mineral compositional relationships in the rock may be interpreted, particularly whether what is observed can be understood in terms of equilibrium having been achieved during the evolution of the rock. Moreover, just *reading* complex phase diagrams is non-trivial.

Total phase diagram is the phase diagram which has *all* the phase equilibria information for a system, ie all the phase assemblage and phase composition dependence on conditions of formation. The number of axes it has, depends on the number of components in the system. For an n-component system, with a particular choice of components, the common choice of the axes is pressure (P), temperature (T) and $n-1$ (independent) compositional (x) ones. There are $n-1$ x terms, because the n'th can always be found by difference; equivalently there are n amounts but only $n-1$ proportions. So there are $n+1$ *axes* to the total phase diagram for a system.

The PTx total phase diagram, is only one of the possible ones, depending on the nature of the system being considered. Variables come in conjugate pairs of intensive and extensive variables:

Intensive variables : i-variables have the same values in all phases which are in equilibrium.with each other, and not on the amount of the components in the system. The main examples are P, T and the μ_i. (The processes for equalisation of these are deformation, conduction and diffusion respectively).

Extensive variables : e-variables, in contrast to intensive variables, depend on the number of moles of the components in the system; they have different values in phases which are in equilibrium.with each other. Examples are entropy (S), volume (V), and the number of moles.(n_i). Defining the mole fraction of i by $x_i = n_i/(\sum n_j)$, x_i can be seen to be a simple function (normalisation) of extensive variables, as is molar volume, $V/(\sum n_j)$, etc.

The conjugate pairs of i- and e-variables are P and V, T and S, and x_k and μ_k. The intensive variable of the pair is the appropriate axis of the total phase diagram *if* the value of that variable can be considered to be constant and superimposed on the system being considered. The P and T variables are the usual choice of axes from these two pairs because deformation and conduction are usually considered to be fast enough geologically for P and T to be considered to be constant and superimposed on the system. If this is not appropriate then the extensive variables need to be used. However V rather than P would be appropriate in order to consider equilibrium for example in fluid inclusions, in which pressure is a passive consequence of the volume of the system (the fluid inclusion), and is not externally superimposed on the contents of the fluid inclusion. Whereas phase diagrams in metamorphic petrology involving V or S are not common, we routinely switch between the extensive and intensive variables of a pair when, for example, we switch from explicitly considered SiO_2 as a composition variable (e-variable) to considering quartz as being in "in excess", with μ_{SiO_2} fixed by the presence of quartz (i-variable).

Given that drawing or looking at even three-dimensional diagrams is difficult, much of the art of phase diagrams has to do with producing lower dimension representations of total phase diagrams. This involves, in particular, various *sections* and *projections* of the total phase diagram. What is possible turns out to depend on the sort of variable involved in a particular axis of the total phase diagram:

Intensive variables as axes : Because all the phases have equal values of the intensive variables at equilibrium, it is possible to *section* the total phase diagram with repsect to intensive variables. Sectioning the total phase diagram is a valuable way of producing a lower dimension representation of the total phase diagram.

Extensive variables as axes : Because all the phases do not have equal values of the extensive variables, it is not possible to section with respect to e-variables. However it is possible to make *pseudosections* with respect to e-variables or functions of e-variables (see below).

Lower dimension representations of the total phase diagrams of which the main types, often used in combination, are projections, sections and pseudosections. Usually the aim is to produce a two-axis representation. A key idea here is the *loss of information* in

going from the total phase diagram to some lower dimension representation. In a sense, the process is one of damage limitation: what information is least needed in the phase diagram? what information is critical? Sometimes several different phase diagrams in combination can provide the necessary detail. Part of the art of phase diagramming is choosing the appropriate phase diagram to draw.

sections of the total phase diagram with respect to i-variables are possible because all the phases have equal i-values at equilibrium. Sectioning can be done at a constant i-value, say constant P or T, or indeed constant PT, or at a function of i-value(s), for example along a PT line, say corresponding to an orogenic PT path. An even more valuable form of sectioning, involving a function of i-values, is when a particular phase is said to be 'in excess', meaning the phase is always present, because this amounts to stipulating a particular value or function of chemical potentials. Clearly the loss of information in going from a total phase diagram to a section involves the dimensions of the total phase diagram used in the sectioning.

Compatibility diagrams are an important sort of section of the total phase diagram, involving sectioning with respect to all i-variables involved as axes of the total phase diagram. The remaining axes of the total phase diagram are all e-variables, and are usually compositional variables. Compatibility diagrams are used quantitatively to represent the phase relationships for the section conditions, and may be calculated or drawn up from the compositions of coexisting minerals in rocks of a range of composition from a small area in the field. Compatibility diagrams are used qualitatively to label fields on, for example, PT projections, representing the topology of the tie lines etc in that field, but not the actual mineral compositions.

projections take the information from a volume of the total phase diagram and project them onto an appropriate plane. The best example is a conventional PT diagram, which should always be called a PT projection; the projection being undertaken with respect to all the compositional variables (e-variables). In other words, the diagram shows the phase equilibria for *all* compositions in the system. Such diagrams must be read with care because not all of the equilibria represented will be 'seen' by each rock. The loss of information in projections has to do with this.disentangling, and with the absence of information on the dimensions of the total phase diagram projected, for example, the phase compositions in the case of PT projections.

It is unfortunate that the term 'projection' is also used for the geometric process of making a phase be in excess in a compatibility diagram context, as in 'projecting' from muscovite in going from $KAlO_2$-FeO-MgO-Al_2O_3 into AFM. Having phases "in excess" amounts to making a *section* of the total phase diagram, and has nothing to do with projections. It is best to avoid using projection in the sense of saying that PT diagram is projected from phase A; much better is to say A is in excess, or just +A.

pseudosection are 'sections' of the total phase diagram with respect to e-variables or functions of e-variables. The most common form is a 'section' for a particular *bulk* composition or range of bulk compositions. Because the compositions of the phases in the system generally lie off the 'section' plane, the diagrams give mineral assemblage information not mineral composition information (ie *pseudo* section). Moreover any open system process that changes the composition of the system generally

invalidates the use of that pseudosection. Regardless of this, pseudosections are invaluable for looking at mineral equilibria, particularly as a way of presenting easily understandable information from PT projections.

In terms of producing lower dimension representations of the total phase diagrams, the choice of axes is critical. Say, a PT projection is to be drawn for the 6-component system, $KAlO_2$-FeO-MgO-Al_2O_3-SiO_2-H_2O; clearly drawing compatibility diagrams for the fields is impossible (4-component compatibility tetrahedra are the largest compatibility diagrams that can be drawn). However, with muscovite, quartz, and H_2O in excess, three components can be treated as μ_i rather than x_i variables, and this 6-component system becomes *effectively* ternary, with (AFM) compatibility triangles now being all that is required. The corresponding PT projection, with muscovite, quartz, and H_2O in excess, will then be a section with respect to the three components treated in terms of μ_i.

Types of phase diagrams : given the difference in properties of intensive and extensive variables it is not surprising that the geometrical relationships on diagrams depend on whether intensive or extensive variables are involved on the axes. On the other hand, if we are looking, for example, at i-i projections—projections with intensive variables on both axes—it will not matter geometrically what combination of P, T and μ_i are involved. Common types of phase diagrams are now outlined, with i used for intensive, and e used for extensive :

e-e sections : mainly compatibility diagrams, as discussed above.

i-e sections : sections with respect to all other intensive variables; can only be drawn for systems which are effectively binary, which have one compositional variable. Examples are T-X and μ_i-X sections. Although a considerable effort is required to make many model systems effectively binary, the rewards are great because the diagrams are generally very illuminating, being able to show the way in which the compositions of the projected minerals change with conditions of formation. Even AFM can be made effectively binary, by having an additional in excess phase, for example biotite.

i-e projections : projections of intensive variable information for effectively binary systems. For example, a P-X projection can show compositional information for equilibria for all temperatures, and, in combination with a standard PT projection, is a valuable summary diagram. Similar diagrams can be drawn for systems larger than effectively binary if there is an identical dominant substitution in all the minerals which are solid solutions. In many systems of interest, $MgFe_{-1}$ is just such a substitution, so that P-X 'projections' can be drawn for AFM for example.

i-e pseudosections : sections with respective to the other intensive variables, but presenting the mineral assemblage information for a line of bulk compositions through the compatibility diagram for the system.

i-i projection : sections with respect to the remaining intensive variables, projections of information involving all the compositional variables. The best example is a conventional PT diagram, but μ-μ diagrams are also in this category. Compatibility diagrams are used to label the fields on i-i projections.

Constructional elements : The different types of phase diagrams have different constructional elements controlled by the different properties of intensive and extensive variables. These elements and the rules which control how they can be put together are now summarised:

i-i projections : the major feature on these diagrams are reaction lines across which compatibility relationships change, by crossing tie lines or disappearance of phase in effectively ternary systems for example. Reactions occur as lines because all the phases have equal values of intensive variables at equilibrium. Reactions generally change stability across intersections; Schreinemakers rules govern the stability relations around intersections in many cases However, where solid solutions are involved, and transitions between systems of different sizes are involved, alternative rules are required. Similarly reactions which reflect singularities, for example when coexisting solid solutions become colinear or coplanar, have to be treated differently.

e-e sections : Compatibility diagrams for an effectively n-component system involve 1-, 2-, and n-phase fields, except at conditions corresponding to reactions or intersections. Fields of coexistence of minerals are involved because extensive variables have different values in coexisting phases at equilibrium. 1-phase fields are always convex in the vicinity of the apices of n-phase fields; they are always of finite size except at a disappearance of phase reaction in which that phase is about to be consumed. Tie lines connect coexisting phases; tie lines can only cross at the conditions of reactions or intersections. Tie line bundles are always of finite width, except at a reaction across which that tie line is broken.

i-e sections : They involve alternating 1-phase and 2-phase fields; in the 2-phase fields, tie lines are at right angles to the intensive variable axis (because intensive variables have equal values in all phases at equilibrium). For the same reason, reactions occur as lines; at each one, three 2-phase fields and one 1-phase field terminates. The metastable extensions of 2-phase field boundaries always lie in 2-phase fields across such reaction lines.

i-e projections : They consist of bundles of lines tracing the compositions of the coexisting minerals along reaction lines
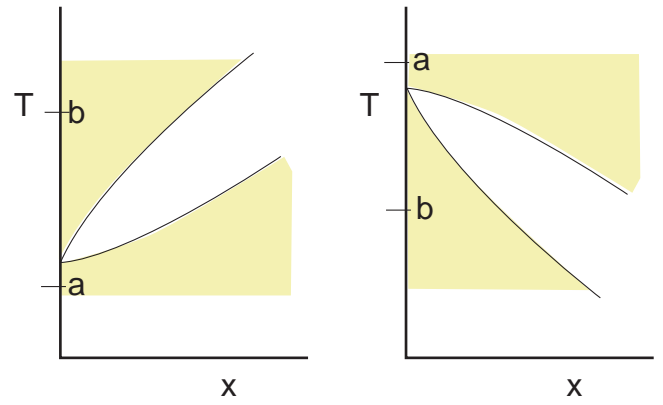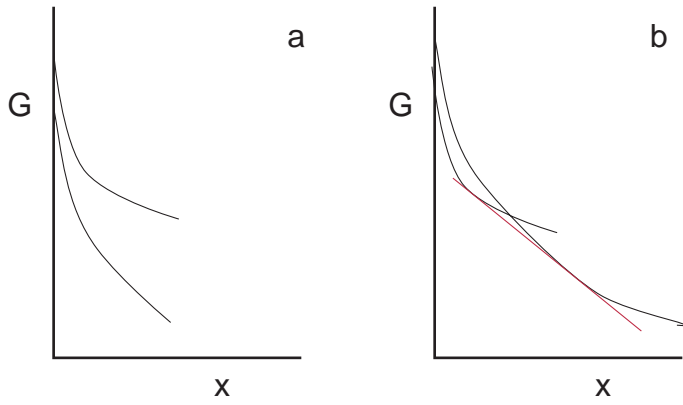
Schreinemakers analysis : i-i projections

This is the approach to follow in sorting out the stability of reactions on i-i projections, for example PT projections. It is not a universal panacea for such diagrams; it does not 'work' for systems involving solid solutions, where there is a reaction connecting a smaller to a larger system, eg reactions connecting KFASH to KFMASH, and where singularities are involved, for example where phases pass through coplanarity with each other with changing conditions. However the method is appropriate for systems with phases of a fixed composition, and for systems with solid solutions which do not involve the above features.

The conventional use of Schreinemakers analysis is to determine which of the reactions are stable and which are metastable where the positions of all the reactions for a system have been calculated. In general, reactions change stability across intersections, Fig. 1,2. In terms of the final i-i projection, only the stable reactions are normally drawn, because these are the only
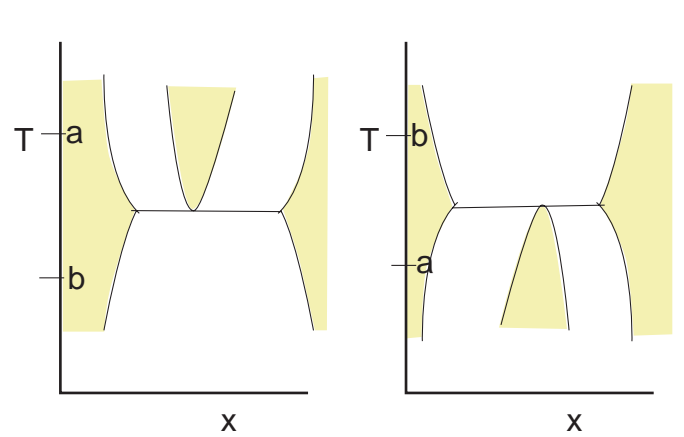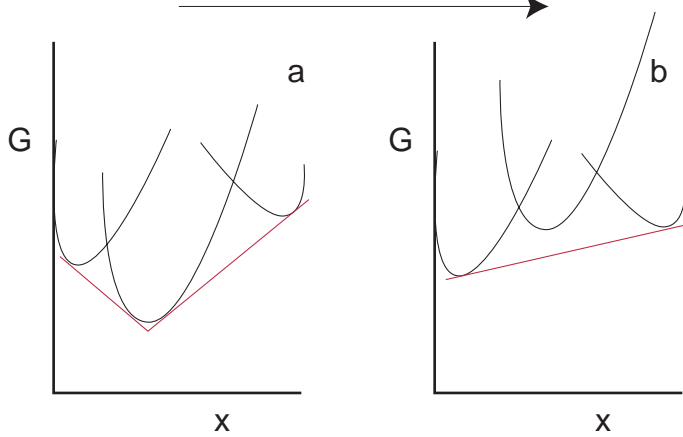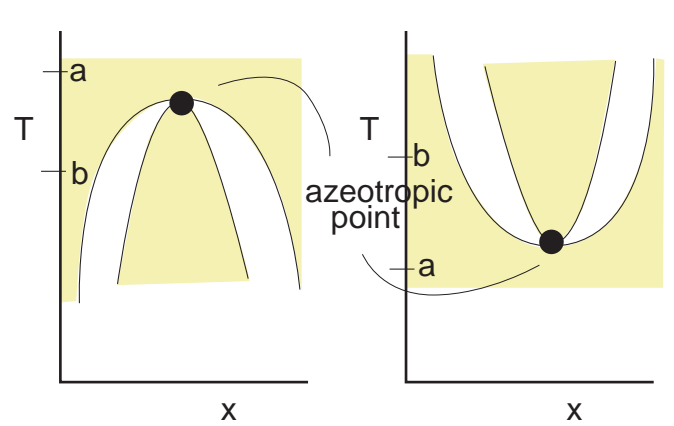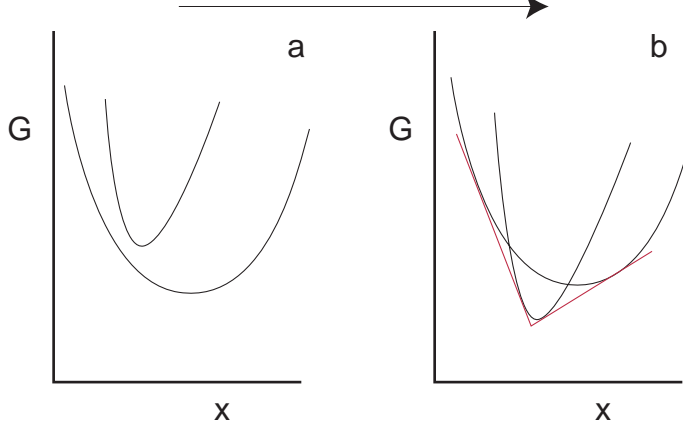
changing T

a

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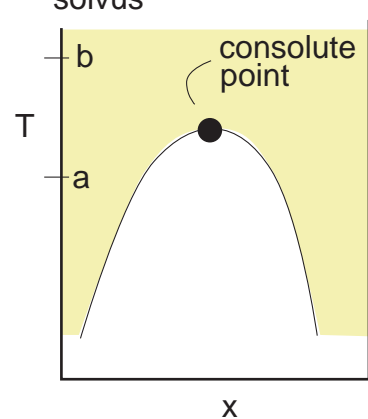increasing T

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Fig. 1 : Schreinemakers analysis applied to the aluminosilicate polymorph unary system

P

[ky]

sill
and

[and]
ky/sill

[sill]

ky
and

ky
and
[sill]

sill
and

ky/sill
[and]

sill
and
[ky]

T

P

[and]
ky/sill

ky

sill

ky
and
[sill]

and

sill
and
[ky]

T

Schreinemakers Rule : the metastable extension of [i] lies between i-producing reactions

Fig 2 : Schreinemakers analysis in AFM : KFMASH + q + mu + H_2O

P

[bi]

st ky
chl g

[st]

chl ky
g   bi

g chl
st bi

[ky]

ky
st g
bi

[chl]

st ky
chl bi

[g]

T

Note that Schreinemakers Rule is obeyed, and that all two phase assemblages
are stable through less than 180¡ through the intersection

ones which can be seen by mineral assemblages which maintain equilibrium, say, with changing PT.

The analysis is done sub-system at a time, starting with the smallest, and intersection at a time. Schreinemakers Rule is usually stated in terms of the 'out' phase for each reaction around an intersection. This works because, for the phases involved in the reactions at an intersection, one phase, in general, is not involved, or 'out', in each reaction. Noting that, for an n-component system, $n + 1$ phases are generally involved in writing a reaction, and $n + 2$ phases are involved in an intersection, there are $n + 2$ reactions around the intersection, each having one phase 'out'. Some reactions involve less than $n + 1$ phases and such reactions are called *degenerate.* When there are degenerate reactions involved in an intersection, less than $n + 2$ reactions are involved around the intersection. For degenerate reactions, more than one 'out' phase is involved.

Schreinemakers Rule gives the *relative* stability of the reactions around an intersection; it says which end of each reaction is more stable than the other end. It is possible for an intersection and all its reactions to be metastable, and, in this case, Schreinemakers Rule gives the different levels of metastability of the ends of the reaction. Having determined the relative stabilities of the reactions around each intersection, putting together the whole diagram involves making consistent the levels of stability of reactions which run between intersections. The stability level of intersections and all their reactions may need to be changed to achieve this. If a reaction running towards another intersection is designated to be metastable, but that intersection designates it to be stable, then that intersection must be metastable, and the reactions around it metastable and very metastable (instead of stable and metastable). The exception to this changing of the stability level of reactions involved in an intersection whose stability level must be changed, is when that reaction is a degenerate reaction from a smaller system (see below). The idea of Schreinemakers Rule providing *relative* stability is important; it is only when the intersections and their component reactions are fitted together that the actual stability of *intersections* can be determined.

Schreinemakers Rule states that *the metastable extension of i-'out', denoted [i], always lies between i-producing reactions* . Looking at Fig. 1-2, observe that this true. When degenerate reactions are involved, say [i,j], then the reaction terminates at the intersection if [i] and [j] are stable on the same side, but the reaction is stable across the intersection if [i] and [j] are stable on opposite sides of the intersection; the former will happen if i and j appear on the same sides of reactions, the latter if i and j appear on opposite sides.

A subsidiary rule is that assemblages involved in sides of reactions can only be stable over 180° or less, and 180° is only possible for degenerate reactions which are stable across an intersection. Look at the stability of ky+g, st+bi, st+chl, etc in Fig. 2 to show that thsi applies. This amounts to a 'consistency' check once the analysis is completed. An even more important check involves going round the final diagram, now involving only the stable reaction lines, and labelling each field with a compatibility diagram, noting that tie lines can only change across a reaction line, and can only change by the specified reaction.

A systematic method should be adopted for performing Schreinemakers analysis. Any system is likely to have reactions occurring wholly in sub-systems, at corners, on edges, on faces of the compatibility diagram for the system. Such reactions must be considered before the full system reactions because their stability is unaffected by the full-system reactions; they will run across full system intersections, and, in fact, a *stable* sub-system reaction can run across a *metastable*

full system intersection! The approach to follow is :

- stage 1 : start by looking at all the constituent 1-component sub-systems, at *apices* of the compatibility diagram. If there are two or more phases plotting at any apex, then do the Schreinemakers for those reaction(s). Remember that in a n-component system, n+1 phases are needed to write a reaction. Note that reactions from different sub-systems will cross indifferently; intersections are not involved.

- stage 2 : now look at all the 2-component systems forming *edges* of the compatibility diagram. If there are any reactions in these sub-systems, do the Schreinemakers on them. Reactions already considered at an earlier stage are unaffected by this stage of the analysis, although those reactions may lie across new intersections; the new intersections may have the same or a lower level of stability than such a reaction. Note that reactions from different sub-systems will cross indifferently; intersections are not involved.

- stage k: repeat for progressively larger systems, until the full system (stage n) is considered.

This scheme may seem laborious but it is the only way to cover all contigencies.

An example : some equilibria in KASH

Looking at Fig.3, appreciate that the compatibility diagram has an inaccessible area, bulk compositions there cannot be considered given that we are not considering any phases in that part of the compatibility triangle. So, in terms of the above systematic approach, the corners of the effective compatibility triangle are cor, or and q.
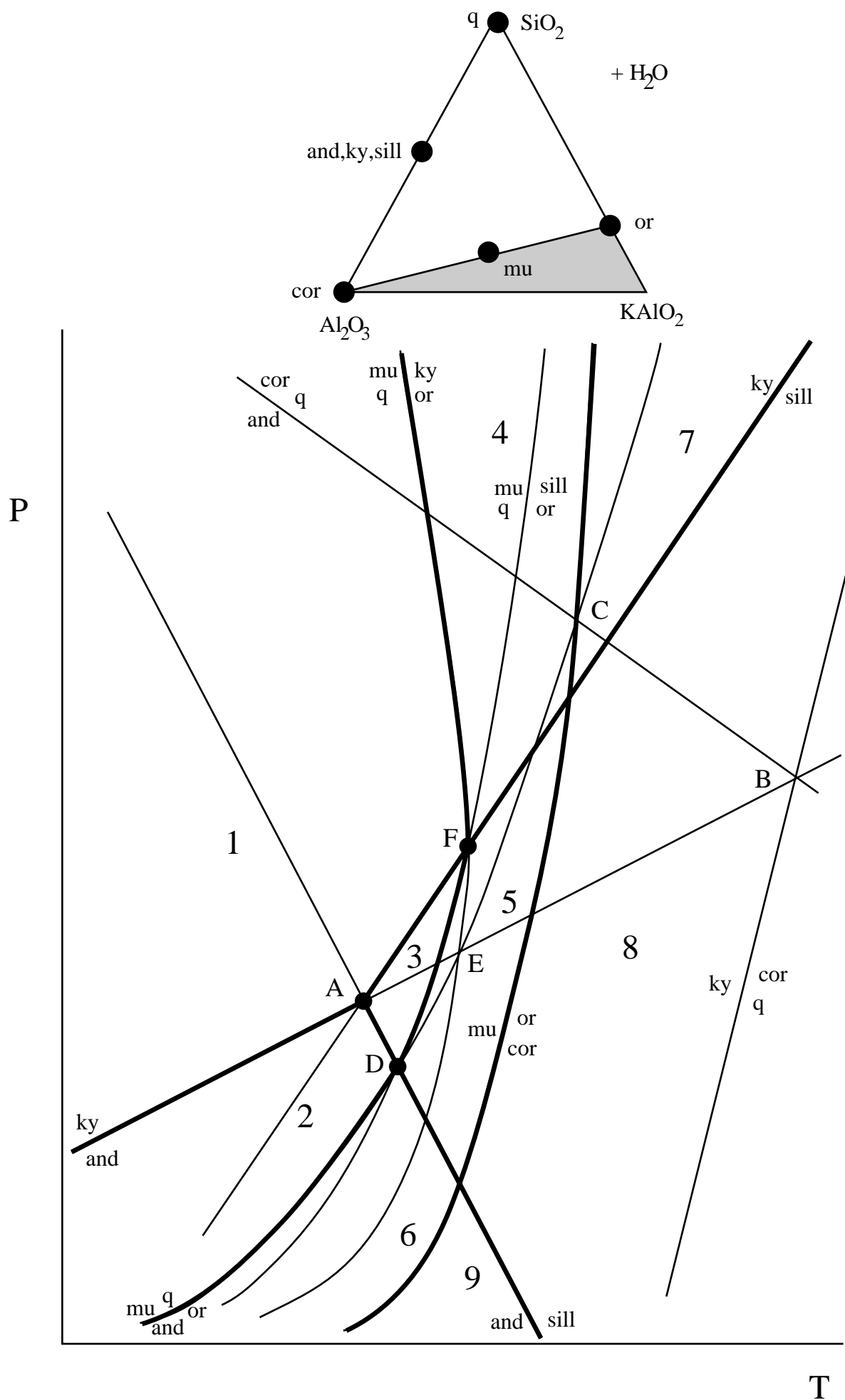
- stage 1 : only one phase at each apex, so no 1-component system reactions. We do know that q, or, and cor must be stable individually over the whole PT diagram because there are no possible reactions which can react them out.

- stage 2 : for two edges of the compatibility diagram there are enough phases to write reactions :

    or-cor : one reaction, cor+or=mu, can be written, and, because there are no reactions in smaller sub-systems, it must be stable along its whole length in the PT diagram,

    cor-q : five reactions : the aluminosilicate polymorph reactions plus reactions of the form cor+q=aluminosilicate. Schreinemakers analysis establishes the stability relations; the aluminosilicate polymorph reactions, although degenerate in this system, do change stability across the triple point, A. The intersection, B, is clearly metastable. Note that these reactions are crossed indifferently at C by cor+or=mu because the reactions are in different systems at the same stage.

- stage 3 : In the full system there are no ternary phases but there are full-system reactions and intersections. The intersections D, E and F involve the ternary reactions, and, in these cases, also reactions considered at an earlier stage. Note that the stability of reactions considered at an earlier stage are unaffected by considerations at this stage.

Fig. 3 : PT projection for KASH (result of Schreinemakers analysis)

C is interesting because, at stage 2 it was an indifferent crossing between two stage 2 reactions, the metastable cor=and+q, and the stable mu=cor+or; now it becomes also a metastable stage 3 intersection involving mu+q=and+or.

- The final stage involves labelling the fields between the *stable* reactions with compatibility diagrams. Note that the accessible part of this triangular compatibility diagram must be covered by triangles. The stable tie lines in a compatibility diagram in a particular field are found by looking at the reactions which bound that field. Remember that tie lines are only changed by crossing reactions. Also, reactions beyond the field of interest may have to be examined, as long as the information they contain is not altered by reactions nearer the field. Look around the compatibility diagrams to do a consistency check.

Additional features

Whereas Schreinemakers 'control' many phase diagram features, in addition there are some other features referred to in the opening paragraph concerning systems with solid solutions. This section serves as an introduction to these; it does not pretend to be complete in covering singularities.
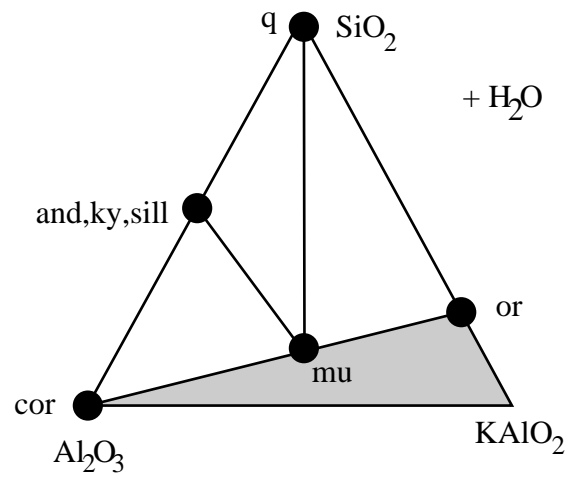
As already explicitly acknowledged above, the heirachy of sub-systems that constitute any system have to be handled in a systematic way in Schreinemakers analysis. This is even more true in handling systems involving solid solutions, for example KFMASH. In such a system, it is appropriate to look first at the constituent sub-systems, and build up to the full system. The new feature is that, when solid solutions are involved, a reaction from the next larger system emanates from each intersection. The intersection, *excluding* this reaction, follows Schreinemakers exactly as before. The additional reaction involves all the phases of the intersection. At the intersection, the phases do not involve any of the additional component, but the proportion of the component increases in the phases in the reaction away from the intersection. The way round of the reaction emanating from the intersection is controlled by the position of the reaction with respect to the reactions making up the intersection; alternatively, if the reaction is known, say from knowledge of the distribution of the additional component between the phases, its position is fixed with respect to the reactions emanating from the intersection.

These ideas can be examined with the help of Fig. 3 which shows the consequence of adding Fe_2O_3 to KFMASH in Fig. 2. The full system reaction emanates from the KFMASH intersection, and the amount of ferric iron in the phases increases away from the intersection along the line. The reaction was located in this position because it is known that ferric iron prefers biotite and staurolite, and thus assemblages involving these phases are stabilised by the addition of ferric iron. The way round of the reaction can be determined by examining AFM + Fe_2O_3, or by observing which phases are 'out' either side of the ferric iron-bearing reaction. This latter method is a powerful control on the geometry of such diagrams.
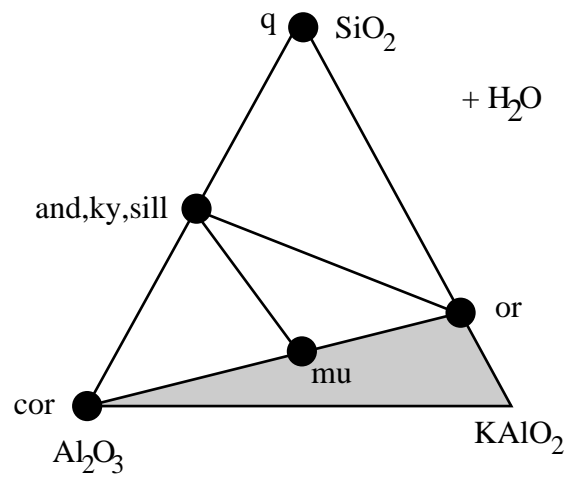
A serious form of complication in phase diagrams involves singularities of various types. Here we will consider just one sort, involving colinearity (coplanarity) of phases in a compatibility diagram, in which at least one of the phases involves a solid solution. The situation is illustrated in Fig.4, showing what would happen if garnet, staurolite and kyanite become colinear in composition *within* AFM. It is supposed that this colinear equilibrium, represented by the colinearity reaction, g+ky=st, intersects the st-g-ky-bi equilibrium in such a way that the

Fig. 4 : compatibility diagrams in the fields of Fig. 3
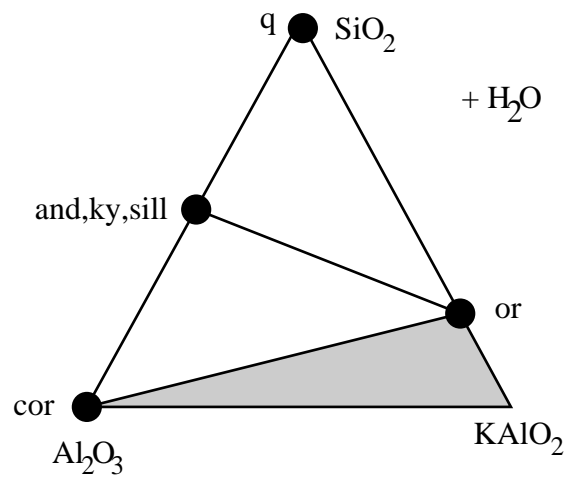   (and, sill or ky as appropriate)

(1,2,3)

q ● SiO$_2$

+ H$_2$O

and,ky,sill ●

or ●

cor ●
mu

Al$_2$O$_3$

KAlO$_2$

(4,6,7)

q ● SiO$_2$

+ H$_2$O

and,ky,sill ●

or ●

● mu

cor ●

Al$_2$O$_3$

KAlO$_2$

(7,8,9)

q ● SiO$_2$

+ H$_2$O

and,ky,sill ●

or ●

cor ●

Al$_2$O$_3$

KAlO$_2$

reaction is st+bi=g+ky at higher pressure, and st=g+bi+ky at lower pressure. The form of such singularities is always like this, with the colinearity reaction terminating at an invariant point (with no metastable extension), with the other reaction changing at the intersection. The details can be understood by examination of the compatibility diagrams; note that the usually the complexities occur over a narrow temperature range. In our calculations singularities of this sort are surprisingly common; it seems to relate to the ability of changing Tschermak's substitutions with pressure and temperature to reverse the Fe-Mg partitioning of elements.
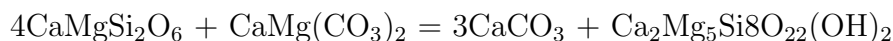
Plotting, balancing reactions, projecting

Plotting phases on compatibility diagrams

Compatibility diagrams are normally plotted in terms of mole proportions (and not volume or weight proportions). Effectively binary systems require a bar diagram to portray compatibility relationships—see Fig. 1. As $MgO:SiO_2$ in chrysotile (chr) is 3:2, this controls the relative position of chr between MgO and SiO2. Thus $MgO/(MgO+SiO_2) = \frac{3}{5}$ so that chr plots $\frac{3}{5}$ of the way between MgO and SiO_2. Obviously chr has more MgO than SiO_2, so that chr plots closer to MgO.

Plotting on ternary compatibility diagrams is essentially the same—see Fig. 2. There are 6 pieces of information with which to fix the composition of a phase, only two of which are independent (ie only two are needed).

Balancing reactions

Reaction coefficients are the numbers before each end-member or phase in a reaction which make the reaction balanced for each component; reaction coefficients are, by convention, negative for end-members/phases on the left of the reaction, positive on the right. So, for :

$4CaMgSi_2O_6 + CaMg(CO_3)_2 = 3CaCO_3 + Ca_2Mg_5Si8O_{22}(OH)_2$

(with H_2O and CO_2 in excess and ignored in the rest of this section), the reaction coefficients are $r_{di} = -4$, $r_{dol} = -1$, $r_{cc} = 3$ and $r_{tr} = 1$. Note that this reaction *is* balanced for CaO, MgO and SiO_2.

Many simple reactions can be balanced by inspection, but for more complex ones, solution of a set of simultaneous equations is involved, each equation ensuring that the reaction is balanced for a particular component. (In excess phases, H_2O and CO_2 here, can be balanced after the other reaction coefficients have been determined, 'in excess' meaning that any quantity of H_2O and CO_2 can be included in the reaction). Using the name of the end-member to represent its reaction coefficient, we will now (re)determine the reaction coefficients for the above equation using the simultaneous equation approach. To balance the reaction for CaO, dol + 2tr + di + cc = 0 must be true, the coefficients in this being the number of CaO in each of the end-member formulae. In this way :

dol + 2tr + di + cc = 0 for CaO
dol + 5tr + di = 0 for MgO
8tr + 2di = 0 for SiO_2

Fig. 1

$+H_2O$

MgO SiO_2

$chr = Mg_3 Si_2 O_{10} (OH)_2$

Fig. 2

$tr = Ca_2 Mg_5 Si_8 O_{22} (OH)_2$

SiO_2

$+H_2O$

Ca:Si
of 2:8

Mg:Si of 5:8

tr

Ca+Mg:Si of 7:8

CaO

MgO

Ca+Si:Mg
of 10:5

Ca:Mg
of 2:5

Mg+Si:Ca
of 13:2

Fig. 3

projection onto cc-ta

$+H_2O+CO_2$

chr'

q SiO_2

ta

tr

dol

q'   tr'

chr
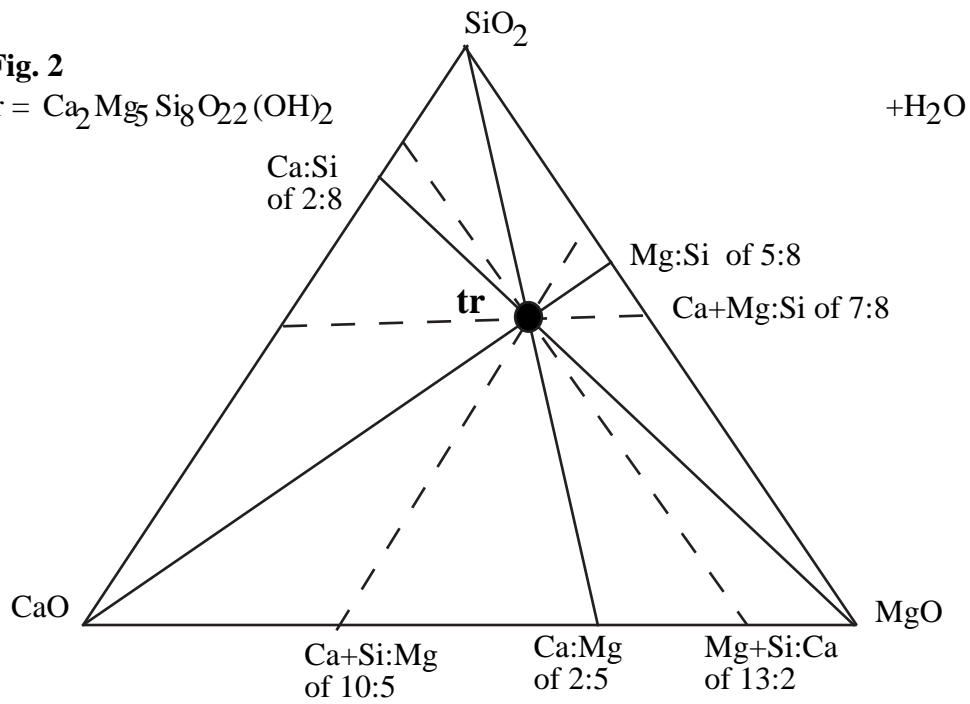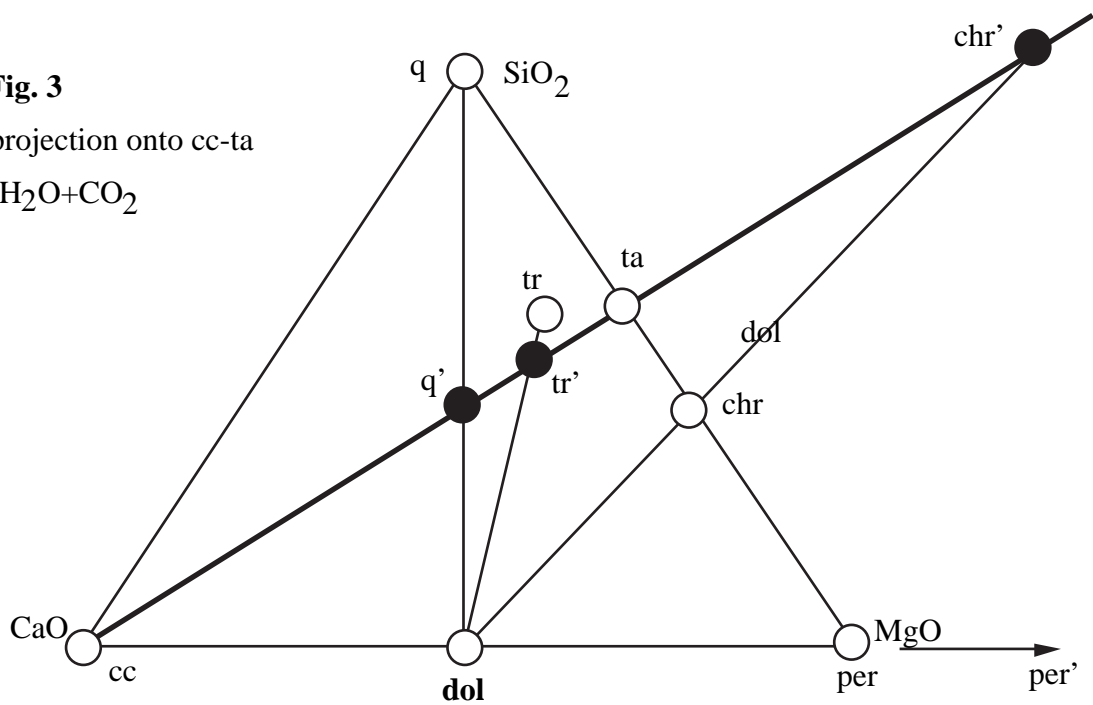
CaO   MgO

cc

dol

per

per'

This is three equations in *four* unknowns, but, in any reaction, all the reactions coefficients can be multiplied by the same arbitrary number, and the reaction is still balanced. So any one reaction coefficient can be set in the above : take tr = 1. Then

dol + di + cc = -2 dol + di = -5 2di = -8

This is trivial to solve, giving : di = -4, dol = -1 and cc =3. In more complex cases a more systematic method, for example Gaussian elimination, is required.

Projections—no solid solutions

We are interested in the graphical construction involved in converting a higher dimension compatibility diagram into a lower dimension one by 'projecting' from a phase or phases, as in converting the 6-component system, $KAlO_2$-FeO-MgO-Al_2O_3-SiO_2-H_2O, into the 3-component AFM by 'projecting' from muscovite, quartz and H_2O. A simple example is illustrated in Fig. 3, involving projection of phases onto calcite + talc from dolomite. Geometrically, it is easy to see what is involved. Algebraically, the method is the same as writing reactions: it involves writing a reaction between the phase to be projected, the phase(s) to be projected from, and coordinates on the line (or plane) onto which the phase is to be projected. In the example in Fig. 3, the coordinates on the line are the phases, calcite and talc.

Considering the projection of quartz in Fig. 3, by inspection, the reaction is

$3CaMg(CO_3)_2 + 4SiO_2 = 3CaCO_3 + Mg_3Si_4O10(OH)_2$

Ignoring the projecting phase, dol, this is 4q = 3cc + ta; where does projected q plot between ta and cc? Care is required - the compatibility triangle involves CaO, MgO and SiO_2, so the points defining the projection line should be expressed in terms of these. $CaCO_3$ involves one molecule (of CaO), but $Mg_3Si_4O10(OH)_2$ involves 7 molecules (of MgO and SiO_2)—note that H_2O and CO_2, being considered to be in excess here, are not included in this calculation. Thus, in terms of *this* compatibility triangle, the reaction is 4q = 3cc + 7ta*, where ta* is talc/7, and projected q lies 0.3 of the distance between cc and ta.

Projecting chrysotile, the reaction is ta + 3dol = 2chr + 3cc, which becomes, ignoring dol :

2chr = 7ta* - 3cc

The negative coefficient for cc means that chr does not plot on the line *between* cc and ta, but on the line *extended*, beyond ta. To see where, consider coordinates along the cc - ta line in terms of ta/(cc+ta) : cc is at 0, ta is at 1 and chr plots at $\frac{7}{4}$.

Projecting periclase, the reaction is dol = per + cc, or per = -cc. Because ta is not involved, per projected plots at infinity, as is clear geometrically.
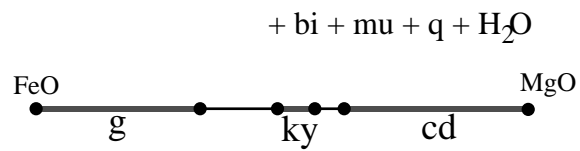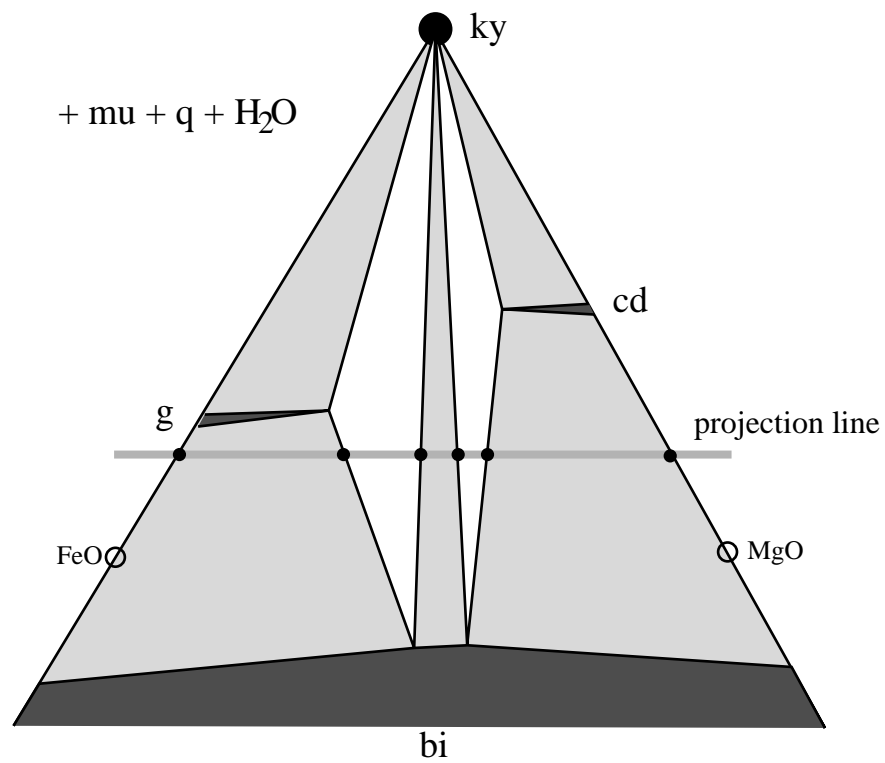
Projections—with solid solutions

When solid solutions are involved, compatibility diagrams, as labels for fields on PT projections for example, may only be drawn qualitatively, showing the basic topology, as the compositions of the coexisting phases vary across the fields. In addition, it is possible to draw quantitative compatibility diagrams from rock data or calculated equilibria for a particular PT for example. Either way, 'projections' are needed to reduce the dimensions of the full compatibility diagram, and inevitably one or more of these phases involve solid solutions.

This involves no particular difficulty although more care and understanding are involved, particularly in choosing a projection line (plane) and in reading the resulting compatibility diagrams. The first, obvious, point is that there is loss of all information concerning compositional variations of the projecting phase; over the resulting compatibility diagram the composition of the projecting phase varies, at least across fields involving less than n phases where n is the number of components involved in the compatibility diagram. In Fig. 4, on projecting from biotite in AFM, the way in which the composition of biotite varies with position across the bar diagram can be seen with reference to the AFM diagram. Clearly it is only across the 3-phase fields in the AFM diagram, and thus the 2-phase fields in the bar diagram, that the biotite composition does not vary. In drawing a quantitative bar diagram at a particular PT from AFM, the projections must be done with respect to the appropriate biotite composition.

A more subtle point about projecting from variable composition phases is that the projection line (plane) should be closer to the projecting phase than the closest variable composition phase. In the AFM case, therefore, the line was chosen to be on the low Al_2O_3 side of garnet. The reason for this is to ensure that, on projection, the compositions of the projected phases vary monotonically across the resulting compatibility diagram. To see that this might not otherwise happen, envisage that for more Fe-rich compositions biotite is more Fe-rich than coexisting garnet, and that for Mg-rich compositions it is the other way round. Then, if the projection line is chosen to be on the high Al_2O_3 side of garnet, then the projected compositions of more Mg-rich garnets will be on the Fe side of Fe-rich garnets

Given this caveat there are often many possible orientations for the projection plane (line); care must be taken in choosing one which illuminates rather than obscures the phase relationships. For example, if Fe-Mg solid solutions are involved then it is wise to have this substitution explicitly in the resulting compatibility diagram. Experiment!

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Fig. 4: projections inv olv ing solid solutions   projection from biotite in AFM

+ mu + q + H_2O

ky

cd

g

projection line

FeO

MgO

bi

+ bi + mu + q + H_2O

FeO   MgO

g   ky   cd

note that the composition of the coexisting biotite
v aries along the bar