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TRUTH AND BEAUTY IN METAMORPHIC PHASE-EQUILIBRIA: CONJUGATE VARIABLES AND PHASE DIAGRAMS

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Abstract

In using calculated equilibria among minerals to understand metamorphic processes, there are usually "natural" choices of axes to use on phase diagrams, depending on the geological supposition of the processes operating in rocks. Thermodynamic variables come in conjugate pairs, intensive and extensive, and the natural choice of which to use as an axis of a phase diagram depends on which of the pair leads to paths for metamorphic processes that are easiest to visualize. An unnatural choice leads to diagrams on which paths are not intuitively obvious, and these diagrams usually have to be calculated. Ideas relating to conjugate pairs are illustrated using mineral equilibria for the upper amphibolite to granulite facies, calculated for an aluminous pelite composition in the system Na_2O–CaO–K_2O–FeO–MgO–Al_2O_3–SiO_2–H_2O (NCKFMASH). We look specifically at the pressure–volume conjugate pair and the H_2O content–aH_2O pair (*i.e.*, the H_2O–μ_{H2O} pair). *P–T versus V–T* and T–M_{H2O} *versus* T–a_{H2O} diagrams are used to consider metamorphic processes. We show that the less obvious variable, for example *V* rather than *P*, may be more useful in considering certain situations, usually transient.

Keywords: mineral equilibria, conjugate variables, partial melting, volume–temperature relationships, activity of H_2O.

Sommaire

Dans l'utilisation des équilibres calculés impliquant les minéraux nécessaires pour comprendre les processus métamorphiques, il y a des choix naturels des axes à utiliser pour construire les diagrammes de phases, dépendant des suppositions faites à propos des processus importants dans les roches. Les variables thermodynamiques se présentent en paires conjuguées, l'un étant intensif, et l'autre, extensif, et le choix naturel à faire dépend de quelle paire mène à un tracé évolutif des processus métamorphiques qui soit le plus facile à visualiser. Un choix non naturel mène à un diagramme pour lequel les tracés ne sont pas évidents de façon intuitive, et un tel diagramme doit en général être calculé. Nous illustrons les concepts liant les paires conjuguées en utilisant les équilibres portant sur les minéraux typiques du faciès amphibolite à granulite, calculés pour une composition représentative d'une pélite alumineuse en termes du système Na_2O–CaO–K_2O–FeO–MgO–Al_2O_3–SiO_2–H_2O (NCKFMASH). Nous examinons tout particulièrement les paires conjuguées pression–volume et teneur en H_2O – *a*H_2O (*i.e.*, la paire H_2O–μ_{H2O}). Les diagrammes *P–T versus V–T* et T–M_{H2O} *versus* T–a_{H2O} servent à évaluer les processus métamorphiques. Nous montrons que la variable la moins évidente, par exemple *V* plutôt que *P*, peut être plus utile dans certaines situations, généralement transitoires.

(Traduit par la Rédaction)

Mots-clés: équilibres de minéraux, variables conjuguées, fusion partielle, relations volume–température, activité de H_2O.

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INTRODUCTION

Much of what is known about orogenesis comes from the study of metamorphic rocks, within the context of the thermomechanical behavior of the outer part of the Earth. The mineral assemblage in a metamorphic rock evolves along a pressure–temperature (P–T) path, the rock possibly changing its composition along the path, for example by addition or loss of fluid or melt. A unifying and simplifying petrological tenet, supported by substantial *a posteriori* evidence, is that a mineral assemblage equilibrates continuously on some scale along a P–T path while fluid or melt is present, but little or no change occurs while fluid or melt is absent. An equilibrium assemblage of minerals will then tend to be preserved once fluid or melt is finally lost, this assemblage reflecting the pressure–temperature conditions experienced when that occurred.

This is a working model for understanding the mineral assemblages and textures preserved in rocks and is justified in part by the success metamorphic geologists have achieved in the last several decades by using it to establish the P–T evolution of ancient orogenic systems.With this model, the full force of equilibrium thermodynamics can be brought to bear on mineral assemblages in rocks as an approach in the investigation of Earth processes. Further, forward modeling to see the consequences of envisaged processes can be undertaken, given a rock composition, a P–T path, and the way that the composition changes along the path.

In phase diagrams, when used to represent the results of forward modeling, there is usually a choice that can be made regarding the axes employed. This choice is commonly made implicitly, without regard to the processes that are being considered. Although phase diagrams drawn with any axes are technically correct, some choices of axes will make the application of the diagrams easier and more informative, at least with the use of appropriate thermodynamic descriptions of the phases, and an appropriate "cartoon" of the processes involved. The purpose of this paper is to explore choice of axes for phase diagrams in the context of the relationship between conjugate pairs of intensive and extensive variables. Mineral-equilibria calculations in the system Na_2O–CaO–K_2O–FeO–MgO–Al_2O_3–SiO_2–H_2O (NCKFMASH) are used to illustrate these relationships.

Consideration of the essential variables for systems, which in the present context are the variables to use for the axes of phase diagrams, is an integral feature of thermodynamics in general (*e.g.*, Munster 1970, Callen 1985). In geology too, various people, not least Dugald Carmichael, have covered this ground (*e.g.*, Thompson 1970, Carmichael 1987, Connolly 1990). We hope to contribute to such discussions in the context of our ability now to calculate phase diagrams relating to the formation of rocks in geologically realistic chemical systems.

AN EQUILIBRIUM MODEL OF METAMORPHISM

Adoption of an equilibrium view of metamorphism is critical in applying equilibrium thermodynamics to rocks, for example in the form of (equilibrium) phase diagrams. There is no disagreement that assemblages of metamorphic minerals are preserved from some part or parts along the P–T paths that they followed, and are out of equilibrium at the Earth's surface. The question is how convolved are the mineral assemblage and information on mineral compositions in a rock stemming from evolution along its P–T path. Can a significant part of a mineral assemblage be identified as substantially reflecting an equilibrium established in some small region along a P–T path? If so, then phase diagrams are potentially useful in metamorphic petrology. Identification of such a mineral assemblage may involve exclusion of minerals occurring as inclusions and thus armored in porphyroblasts, and minerals produced by retrogression. If equilibrium compositions of minerals are also to be identified, then prograde and retrograde zoning of the minerals has to be taken into account, for example.

The following summarizes a simplistic macroscopic view of equilibration in a mineral assemblage following a P–T path that corresponds in most ways to commonly held, if sometimes implicit, views of metamorphism. It has the merit of leading to a mineral assemblage that can have a significant part that does reflect an equilibrium established at a particular P and T. Nucleation and diffusion are the essential processes involved in equilibration. Given a mineral assemblage, diffusion leads to the development of equilibrium compositions of minerals on a length scale that depends primarily on temperature and time available, as well as grain size, given that grain-boundary diffusion is generally faster than intracrystalline diffusion. Such an equilibration volume may not include the core of minerals with relatively slow rates of intracrystalline diffusion. Grain boundaries that are fluid- or melt-bearing are usually considered to lead to faster intergranular diffusion than ones without. As diffusion rates are an exponential function of temperature, the size of equilibration volumes are strongly temperature-dependent.

An assemblage with equilibrium compositions of minerals is in stable equilibrium only if the assemblage is the lowest Gibbs energy one (in a constant superimposed P–T environment; see below). With changing P and T, continuously maintained equilibrium between the minerals can become a metastable equilibrium if nucleation has not occurred to introduce a mineral required for the assemblage to be stable. For each mineral, nucleation rate will be dependent on ΔT, the extent of overstepping of the new mineral's appearance in terms of T, as well as the presence of appropriate sites for nucleation and plausibly the presence of fluid or melt. Although there is no reason to suppose that temperature overstepping is significant, nevertheless the commonplace growth of porphroblasts that are large compared with the matrix grain-size suggests that nucleation is not always easy, but that grain growth on few nuclei compensates for it.

Considering metamorphism with increasing temperature of a first-cycle metamorphic rock (*i.e.*, one that has not seen a previous metamorphic cycle, so is hydrous and fluid-bearing), it is reasonable to suppose that there is a continuous overprinting and destruction of previous assemblages of minerals, as progressive dehydration occurs, with stable equilibrium assemblages and mineral compositions more or less continuously maintained (*e.g.*, Carmichael 1969). This is the first important step in the development of an equilibrium model: that there is commonly a mineral assemblage toward the peak of metamorphism that reflects a stable equilibrium.

The second step involves the "switching off" of this progressive metamorphism such that the mineral assemblage is preserved. The primary cause of this preservation is the transition from the presence to an absence of fluid or melt, stemming primarily from the role of open-system processes during metamorphism, specifically the loss of fluid and melt (*e.g.*, Guiraud *et al.* 2001, White & Powell 2002). Nucleation and diffusion also contribute: for example, with cooling, rapidly slowing diffusion superimposed on a higher-temperature grain-size restricts the effect of continued diffusive equilibration. This effect is compounded by the absence of a fluid or melt on grain boundaries. A more subtle effect is possible; once fluid or melt are gone, a rock with a fixed composition (specifically, fixed H_2O content) generally experiences limited change in mineral assemblage on cooling (unless H_2O is added externally during the retrograde history), compared with the changes on heating associated with rapidly changing H_2O content of the mineral assemblage as fluid or melt loss occurs.

We argue that such an equilibrium model is applicable to many mineral assemblages, with care being required regarding preserved prograde features (specifically, growth zoning of minerals), and diffusive change in mineral composition after the main assemblage of minerals has been "frozen in" (for example, retrograde zoning). It is worth noting that in much forward modeling using pseudosections (see below), it is the preserved *assemblage* of minerals, in some cases their proportions, that are of interest, rather than specifically the mineral compositions corresponding to the preserved assemblage. In this case, a particularly strong case can be made for the equilibrium model. Nevertheless, it is not straightforward to identify and find the composition of the equilibrium volume for forward calculation of mineral equilibria, a serious practical concern in modeling rocks. There is thus a danger that textural features or processes are described as being "disequilibrium" where there has simply been an incorrect identification of the equilibration volume. Alternatively, some textural features commonly interpreted in terms of disequilibrium can also be accounted for by equilibrium processes (*e.g.*, White *et al.* 2002).

A sharper form of the equilibrium model involves mineral *compositions*, as well as the mineral assemblage, being "frozen in". In that case, calculated isopleths can be compared with the observed compositions of minerals that are interpreted to have been the equilibrium ones, for example, to more closely tie down metamorphic conditions. However, the importance of the weaker form of the metamorphic model is that forward modeling provides useful results even if only the equilibrium assemblage of minerals can be identified, where likely equilibrium compositions cannot be established, for example in the situation where several minerals are zoned or there is substantial equilibration of the minerals during cooling.

CONJUGATE PAIRS OF THERMODYNAMIC VARIABLES

There are two sorts of thermodynamic variables: intensive and extensive. Intensive variables in different parts of a system at equilibrium are identical: this is a property called contact equilibrium (*e.g.*, Munster 1970). Equilibration within a system involves equalizing the intensive variables: temperature by conduction (possibly with convection), pressure by deformation, and chemical potentials by diffusion. In contrast, extensive variables depend on the amount of material: volume, V, entropy, S, and composition, n_k. Each of the extensive variables can be considered in a form normalized to the number of moles of material in the system, Σn_i, giving molar volume, molar entropy and mole proportion, x_k. Note that Prigogine & Defay (1954), for example, also call such normalized variables intensive variables, in addition to the contact equilibrium ones, requiring only that intensive variables do not depend on the amount of material involved. Theirs is not a helpful usage in the current context of conjugate pairs of variables.

The variables come in conjugate pairs, T and S, P and V, and μ_k and n_k. Phase diagrams may involve one or other of each of the conjugate pairs. In the fundamental thermodynamic description of a system without external constraints applied, the internal energy of the system, U, is minimized, the controlling variables being S, V and n_k, with the corresponding intensive variables being passive ones. For example, such a system held at fixed S and V will come to equilibrium by varying T and P, the implication being that the environment of the system does not control or superimpose T and P on the system.

The roles of controlling and passive variables can be swapped, formally, by performing the appropriate Legendre transform on the internal energy (*e.g.*, Munster 1970, Alberty 1997). Applying a Legendre transform to U with respect to an intensive variable, i, means that the system is now considered to come to equilibrium at constant superimposed *i*, with the corresponding extensive variable, *e*, now passive. The energy minimized at equilibrium is now this transformed energy. Thus for the usual *P–T* world assumed in much of metamorphic geology, the internal energy is transformed with respect to *P* and *T* (making the Gibbs energy, *G*), and such systems are considered to come to equilibrium at constant superimposed *P* and *T*. This assumption requires that the environment of the system allows the necessary change in volume (by it deforming) and entropy (by heat flow) for the *P* and *T* of the system to be maintained.

For an *n*-component system, there are $n + 1$ independent variables, involving either the intensive or the extensive variable in each of the $n + 1$ conjugate pairs. A $(n + 1)$-dimensional phase diagram, coined a *total phase-diagram*, contains all of the information for the system. Depending on the choice of independent variables, there are 2^n different total phase-diagrams. For $n > 2$, the total phase-diagram cannot be drawn, and representing information from it can be done only with projections and sections (*e.g.*, Kroger 1973, Powell *et al.* 1998). In projections, information from throughout the total phase-diagram is "projected" onto one of its faces: the most familiar one is the *P–T* projection (or petrogenetic grid).

In sections *sensu lato*, as the name implies, the two-dimensional representation is a "cut" through the total phase-diagram. For such a cut, $n - 1$ variables must be specified. A section *sensu stricto* results if these $n - 1$ variables are all intensive, so that all the phases are in the plane of the section as a consequence of contact equilibrium; otherwise, the diagram is referred to as a *pseudosection*, signaling that the phases are not all in the plane of the section (as in the experimental petrology term, pseudobinary). [The term pseudosection seems first to have been used in (unpublished) lecture notes for a Mineral Equilibria course taught by RP in 1986 at the University of Melbourne]. The most common form of pseudosection is one in which the $n - 1$ variables specify the system's composition (*i.e.*, they are extensive), and the two variables plotted are *P* and *T*, yielding a *P–T* pseudosection. The variables specified and plotted, however, can be in any combination; all combinations of intensive and extensive variables make possible axes. For an *i* axis, phases at equilibrium all have the same value of the *i* variable (*via* contact equilibrium), whereas for an *e* axis, this requirement does not apply.

A pseudosection can be drawn for any choice from each pair of conjugate variables, regardless of which are the controlling variables that the actual system experiences. If a pseudosection is drawn with a particular *i* axis, however, and the corresponding *e* variable is the controlling one in the system of interest, it will be diffcult to read, although the diagram will be "correct". This is because the variable in the axis is passive in the actual system, so will vary as a consequence of the behavior of the controlling variable. This drawback is easier to see with examples.

In the following two sections, we look at corresponding pairs of phase diagrams (*sensu lato*, including pseudosections) pertaining to an aluminous metapelitic bulk-composition in the system Na_2O–CaO–K_2O–FeO–MgO–Al_2O_3–SiO_2–H_2O (NCKFMASH). The *P–T* pseudosection for upper-amphibolite- to granulite-facies conditions for this rock is given in Figure 1, its composition being given in the figure caption. The calculations were performed with the software THERMOCALC3.22 (Powell *et al.* 1998), using the same datafile (*i.e.*, activity–composition relationships of the phases) and an internally consistent thermodynamic dataset as used by White *et al.* (2001) and Holland & Powell (1998, and upgrades: version 5.2). The lowest variance fields are the narrow divariant fields, with the one corresponding to the bi + sill = g + cd + liq KFMASH univariant reaction (with q, ksp and pl in excess) representing the amphibolite- to granulite-facies transition in the model system. The abbreviations used are given in the caption to Figure 1. The solidus lies between 650° and 680°C for this H_2O content of the bulk composition, chosen such that the mineral assemblages are just H_2O-saturated at the solidus above 3.5 kbar (*e.g.*, White *et al.* 2001).

THE PRESSURE–VOLUME CONJUGATE PAIR

The pressure–volume conjugate pair is interesting in that it is possible, at least transiently, for real systems not to operate at constant superimposed pressure (*e.g.*, Carmichael 1987). In that case, the standard *P–T* pseudosection approach might hide interesting aspects of the way rocks evolve. Instead of a *P–T* pseudosection, a *V–T* pseudosection is needed. Figure 2a shows the *P–T* pseudosection contoured for molar volume, and Figure 2b, the *V–T* pseudosection generated from it. The volume includes fluid and melt as appropriate. This figure is contoured for pressure, and the positive ΔV aspect of all the divariant fields and the majority of the other lower-variance fields is evident. The volume change at constant pressure in the higher-variance fields is generally small and positive.

Metamorphic-process-related issues regarding *P* and *V* are considered in Figure 3, enlargements of the appropriate parts of the *P–T* and *V–T* pseudosections relating to muscovite + quartz melting. This melting reaction has been investigated experimentally by Rushmer (2001), who inferred that the large change in volume has a strong influence on melt loss. On the conventional *P–T* representation, there is a considerable (positive) change in volume across the narrow muscovite + quartz melting field. For a *P–T* pseudosection to be the "natural" phase-diagram to represent muscovite + quartz melting, one has to assume that the environment of the rocks in which this melting reaction is occurring is able to deform quickly enough to allow the melting rock to maintain constant pressure. Transiently, this requirement may not be achieved.

In this transient case, the melting relationships can be looked at more easily on the *V–T* diagram (Fig. 3b). On meeting the divariant field, K-feldspar starts to grow, and the melting step associated with muscovite + quartz breakdown commences; there are three end-member possibilities for the *P–T–V* evolution:

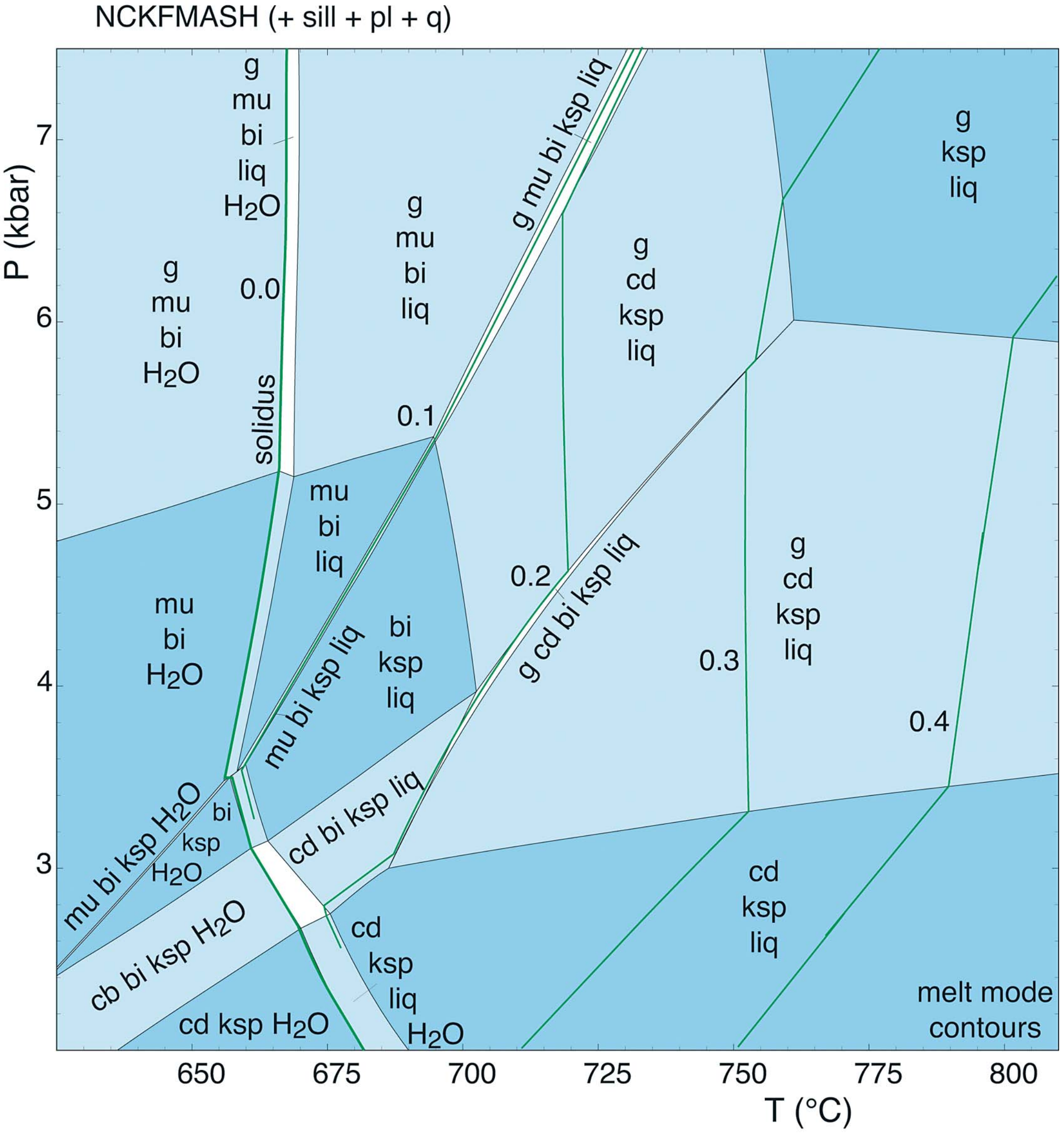


FIG. 1. *P–T* pseudosection for an aluminous metapelite with a composition in the system NCKFMASH; in mole %, it contains 0.97 Na_2O, 0.66 CaO, 2.42 K_2O, 6.26 FeO, 2.09 MgO, 15.38 Al_2O_3, 65.91 SiO_2, and 6.33 H_2O. The phases that are "in excess" for this composition (*i.e.*, are present in every field of the diagram) are sillimanite, plagioclase and quartz. The H_2O content was chosen such that the calculated assemblage of minerals is just H_2O-saturated at the solidus above 3.5 kbar. The contours are melt modes (phase proportions, calculated on a one-oxide basis). Omitted for simplicity are phase relationships involving kyanite and staurolite in the top left-hand corner of the figure. Symbols used are: q: quartz, pl: plagioclase, ksp: K-feldspar, mu: muscovite, bi: biotite, g: garnet, cd: cordierite, opx: orthopyroxene, sill: sillimanite, and liq: silicate melt.

(1) The standard interpretation, that the rock stays at 6 kbar, with the implication that the rock's environment deforms to accommodate the volume increase, is shown by path a on Figures 3a and 3b. In this case, the *P–T* pseudosection is the logical phase-diagram to use, as the rock's evolution can be shown as a horizontal line.

(2) The closed system interpretation at constant volume involves a transient increase of pressure, shown by path b. As drawn, the arbitrary supposition is that once an overpressure of 0.5 kbar is reached, the system relaxes, path c, returning the rock to 6 kbar. The relationship of the melt-mode contours to the a and b–c paths on Figure 3b shows that in the latter case, the melting step associated with muscovite + quartz breakdown is slightly wider in *T* compared to the former.

(3) The open system interpretation is that the rock follows a path close to path a, for example path d, with the volume change required to maintain this pressure

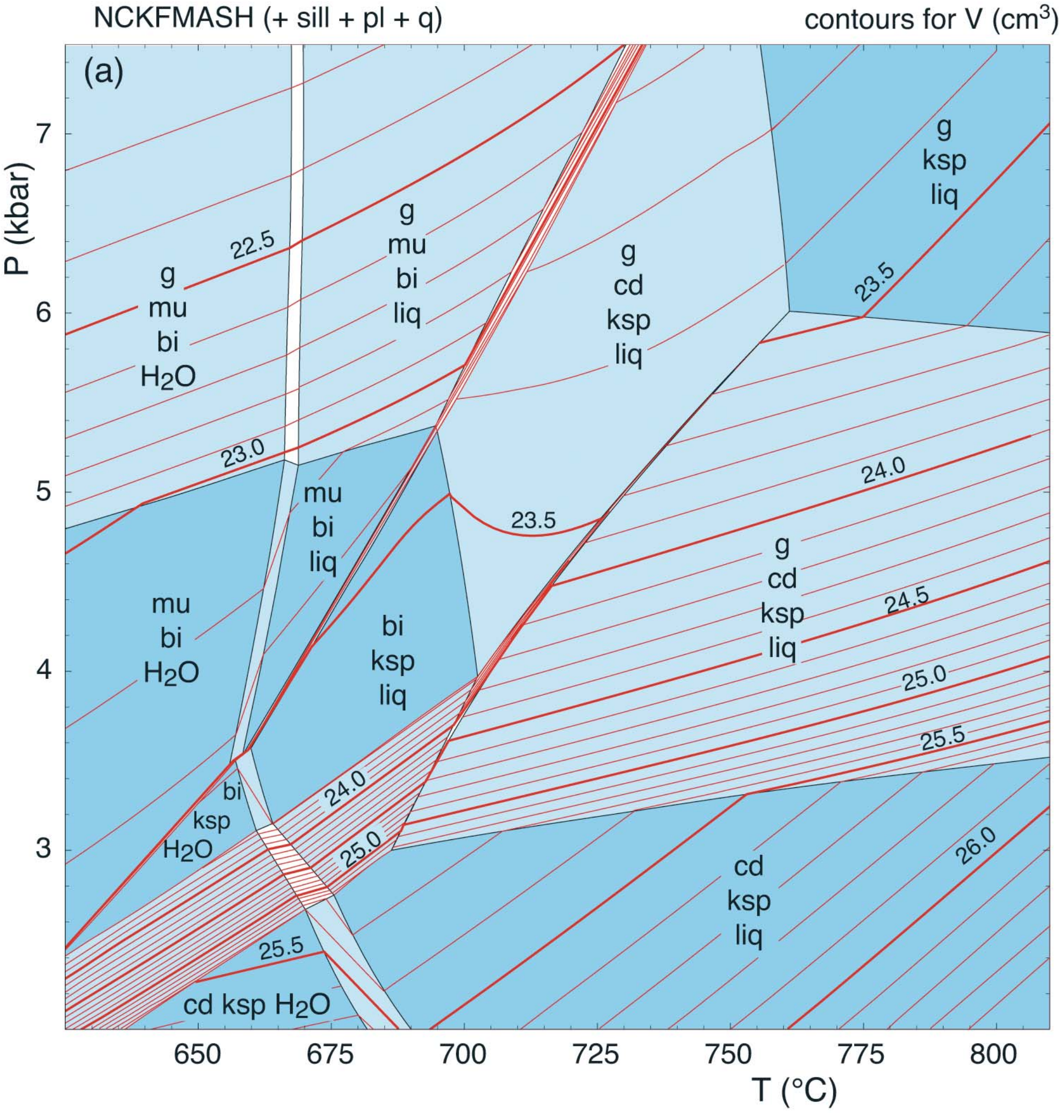
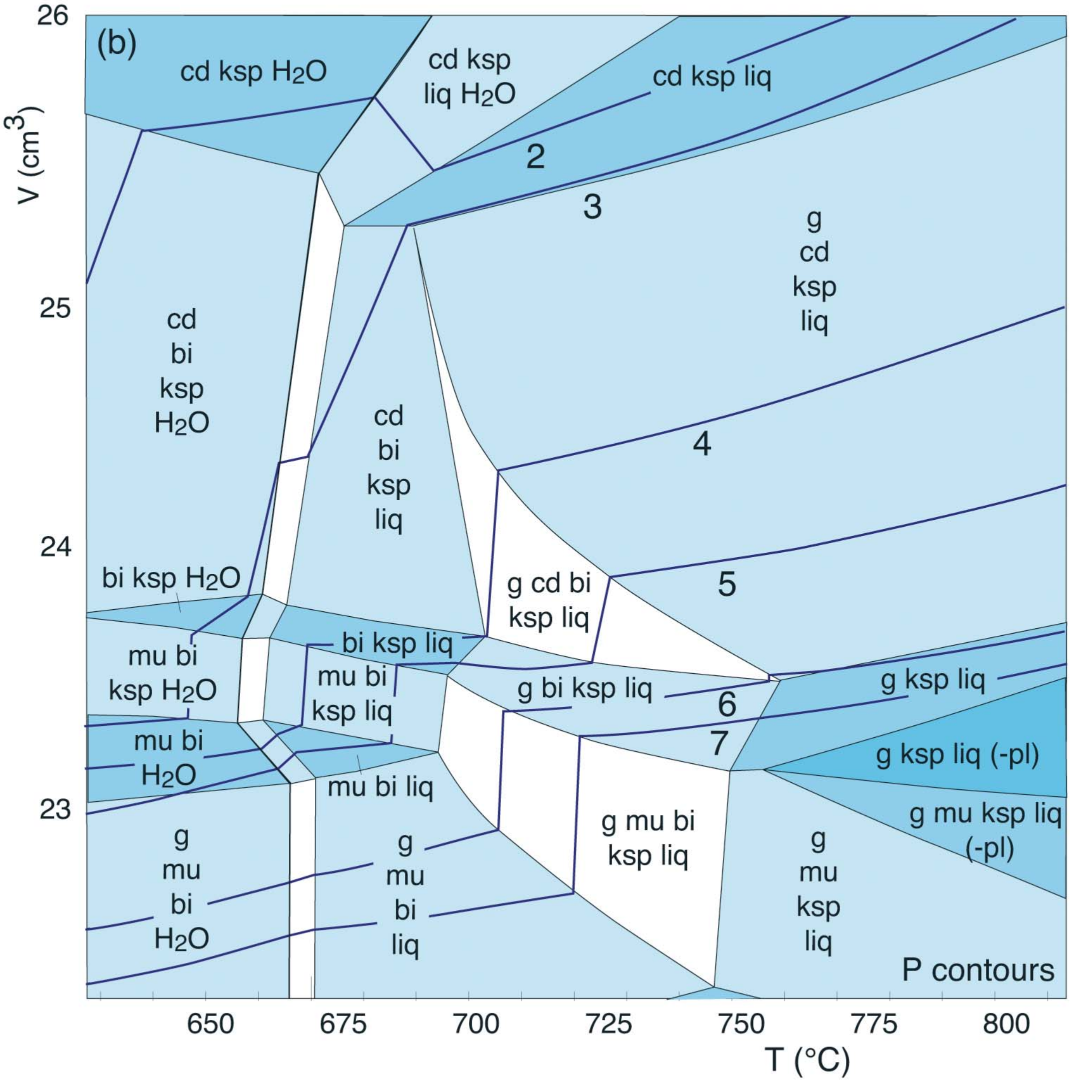


FIG. 2. (a) The *P–T* pseudosection of Figure 1 contoured for molar volume (in cm^3). The bulk composition is given in the caption for Figure 1. On such a diagram, in the absence of univariant lines, volume is piecewise continuous in *P–T*. (In THERMOCALC, volumes are calculated *via* the datafile script, "calcv"). (b) The corresponding *V–T* pseudosection to (a), contoured for pressure. The bulk composition is given in the caption for Figure 1. The notation "-pl", used for the two fields at high temperature, indicates that plagioclase is not present in these fields.

being accommodated by melt loss from the rock. In this case, the rock, in changing composition, leaves the plane of this pseudosection: strictly, the path cannot then be portrayed on Figure 3b. However, as melt is lost, the line where muscovite + quartz react out will change little, and the total amount of melt produced will be very similar to case (2), as this will be controlled primarily by the overall mode of muscovite.

There are various intermediate cases between these end-member possibilities. Path b' is drawn on the assumption that the small change in volume with *T* involved in reaching A in Figure 3b from lower *T* can be accommodated by deformation in the rock's environment, and that this volume change can be continued beyond A. Path e is drawn for the case where melt production is faster than melt escape, requiring a greater transient increase of pressure to drive it.

Open-system cases are interesting in light of the necessity of melt loss to account for preservation of mineral assemblages at high metamorphic grade (*e.g.*, White & Powell 2002). This provides a ready mechanism to "pump" melt out of rocks that are crossing low-variance fields across which there are significant increases of volume. For such a process to occur, there must be appropriate physical conditions, related for example to melt connectivity, rock rheology (so that the matrix can collapse behind the departing melt), and a porosity outside the rock into which the melt can go.



If the change in volume across the low-variance field is negative, as for example at low pressure across the solidus in Figure 2b, then the corresponding situation to the third possibility is that the rock becomes a sink for melt from elsewhere, allowing the rock to maintain the pressure of its environment. Alternatively, the rock becomes a locus of deformation. (The magnitude of the effect implied in this specific example is unrealistic, as the bulk composition for which this diagram was drawn is for H_2O saturation at the solidus in the muscovite + quartz stability field. Thus here the H_2O content of the rock is rather large at the solidus).

Figure 2b is also relevant in the consideration of mineral equilibria in rocks within which boudinage is occurring. In this case, it is interesting to think of this process in terms of volume being increased, rather than pressure being decreased. Leucosomes are common in such locations. Although this is just the sort of site to which melt might migrate in possibility 3 above, it is interesting to observe using Figure 2b that a volume increase can promote *in situ* melting in boudinage necks, as would happen for example for a rock in the bi + ksp + liq field in Figure 2b being boudinaged.

The transient effects discussed above are only likely to be significant if the volume change with temperature

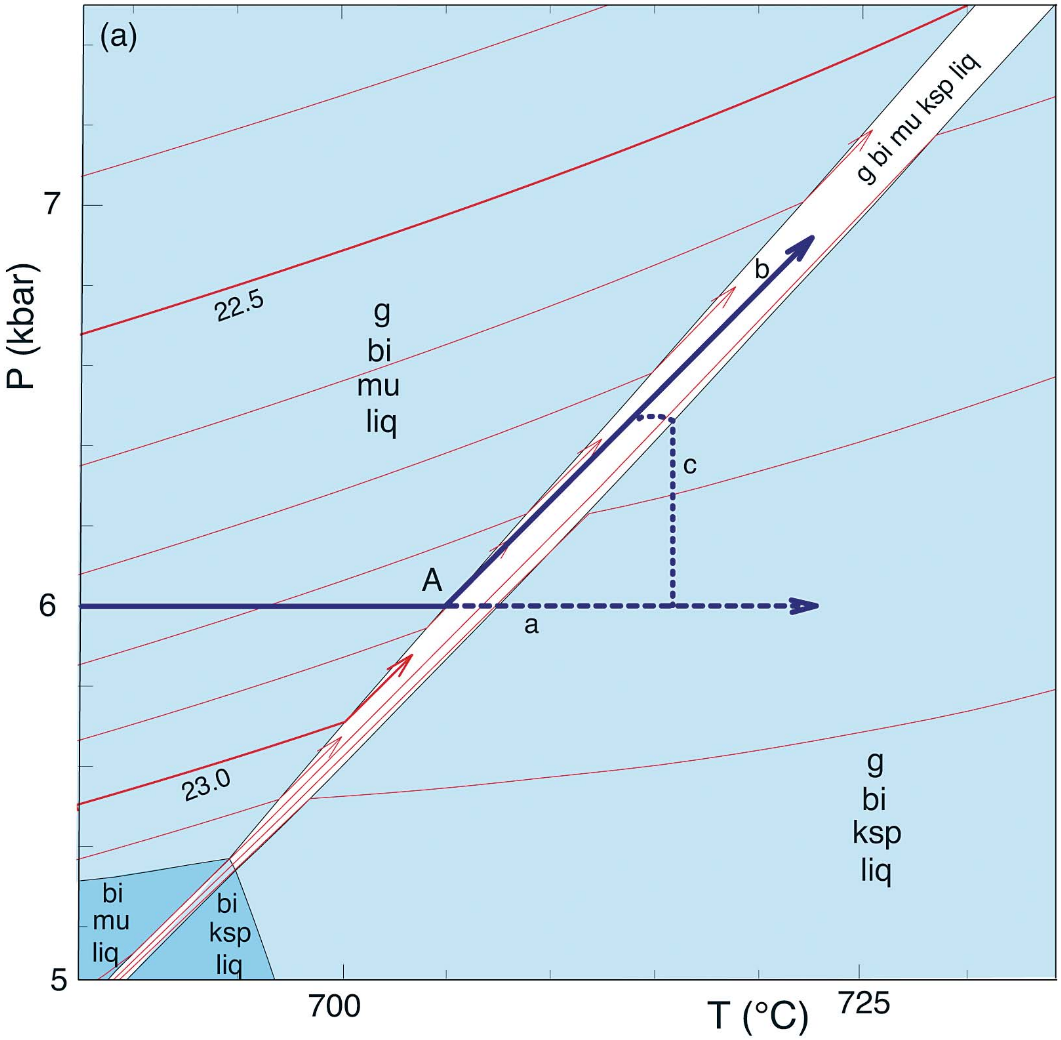


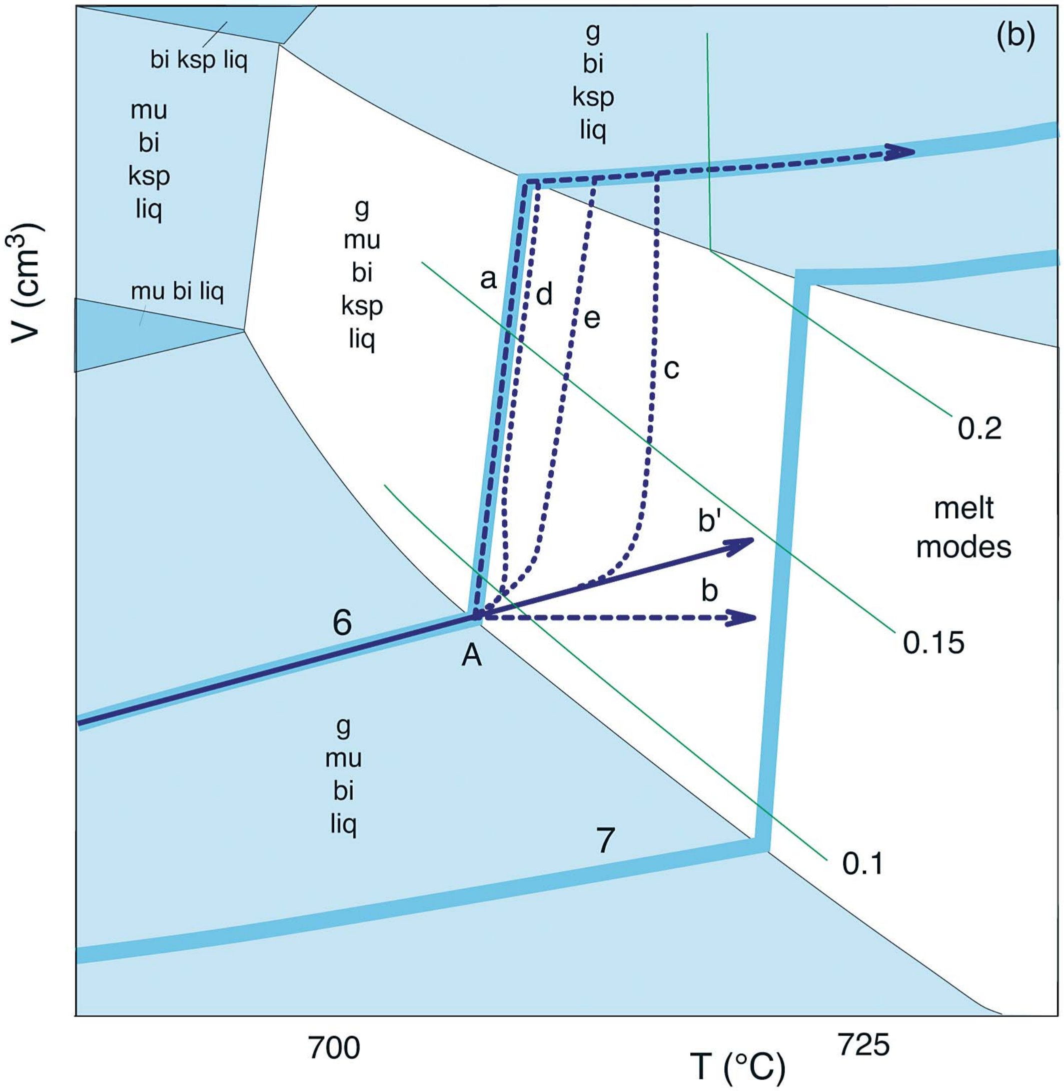
FIG. 3. Enlargements of corresponding parts of the *P–T* and *V–T* pseudosections relating to muscovite + quartz melting across the g + bi + mu + ksp + liq divariant field. The arrowed lines and labeling relate to postulated processes discussed in the text.

as modes change is relatively rapid, as across the low-variance fields in Figure 2b.

The H_2O Content – H_2O Activity Conjugate Pair

The conjugate pair argument is particularly clear regarding "composition" variables, for example considering H_2O in metamorphic processes. The choice, in terms of phase-diagram axes, is now between the amount of H_2O, M_{H2O}, the H_2O content of the mineral assemblage (*i.e.*, the structural H_2O in the minerals plus the H_2O in a fluid or melt, or both, if present), or the activity of H_2O, a_{H2O}, or equivalently the chemical potential of H_2O, μ_{H2O}. In the following, a fluid, if present, is assumed to be pure H_2O.

The activity, a_{H2O}, is the controlling variable only if the system being considered involves variations in the activity, for example as the system comes to equilibrium, or if a_{H2O} is superimposed on the system. In addition, metamorphism under subsolidus conditions of fluid-present mineral assemblages, in which fluid generated by dehydration reactions is largely lost, involves aH_2O as effectively the controlling variable (at a fixed value of $a_{H2O} = 1$), with M_{H2O} decreasing as fluid is lost. In fluid-absent systems, including at suprasolidus conditions, it is generally the amount of H_2O, M_{H2O}, that is



the controlling variable. The usual context, in having the H_2O content as the axis of a phase diagram, is to consider the axis involving a fixed anhydrous rock composition, to which H_2O is then added. Such an axis is designated as M_{H2O} (Guiraud *et al.* 2001).

In Figure 4, a_{H2O} contours are superimposed on a situation where the rock is at a fixed H_2O content M_{H2O} = 0.22 (for the scale of M_{H2O}, see the caption to Fig. 5), so a_{H2O} is the passive variable.The a_{H2O} decreases toward higher temperature, reflecting the affinity of H_2O for melt and the increasing modal proportion of melt to higher *T*.

On a T–M_{H2O} pseudosection (Fig. 5), a rock heating or cooling at a fixed H_2O content moves on a vertical line. Whereas on this figure, the passive variable above the solidus, a_{H2O}, decreases to high temperature, below the solidus it decreases to low temperature to the left of the H_2O saturation line. This pattern results in an unusual feature of this figure: the a_{H2O} contours focus in on the very narrow mu + bi quinivariant field at lower

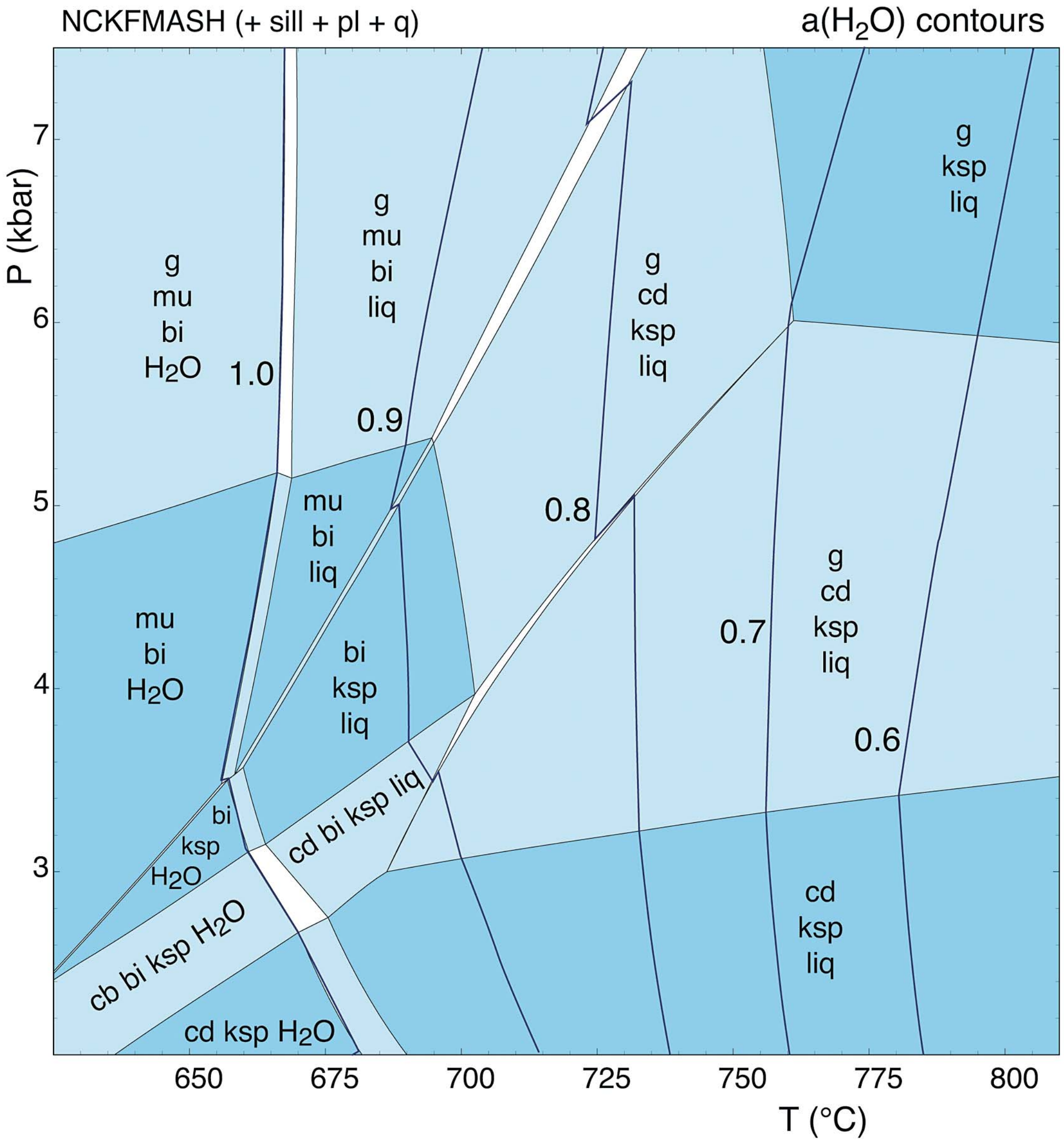


FIG. 4. The *P–T* pseudosection of Figure1 contoured for activity of H_2O (a_{H2O}). The bulk composition is given in the caption for Figure 1. On such a diagram, a_{H2O} is piecewise continuous in *P* and *T*.

temperature (at 650°C, width in M_{H2O} is 0.2049–0.2080, but a_{H2O} is 0.64–1).

On the corresponding T–a_{H2O} pseudosection, Figure 6, lines of constant M_{H2O} also are shown, the labels corresponding to the arrows along the *x* axis of Figure 5. With the composition variable M_{H2O} being converted into an intensive variable for this figure, divariant fields in Figure 5 become divariant reaction-lines here. For example, the divariant field bi + g + cd + ksp + liq, marked A in Figure 5, becomes the reaction line marked A in Figure 6. The reaction that occurs across this line depends on whether a_{H2O} is considered to be the active variable (*i.e.*, a_{H2O} is superimposed on the system): bi + liq = g + cd + ksp, or whether the

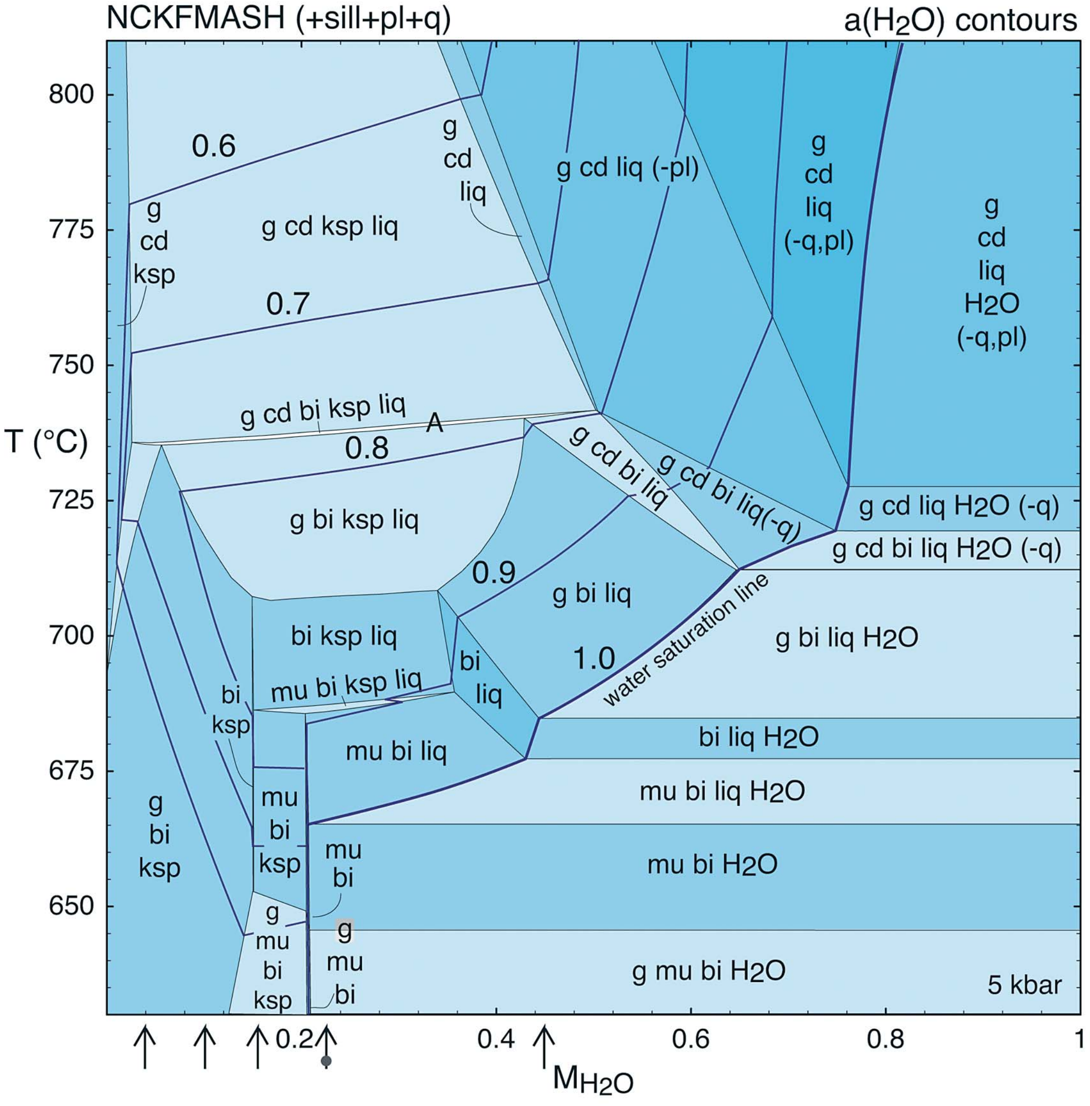


FIG. 5. The T–X pseudosection, in which the x axis, designated M_{H2O}, takes the anhydrous equivalent of the bulk composition in Figure 1 and adds H_2O to it. M_{H2O} has an arbitrary scale running from 0 to 1, with the H_2O for $M_{H2O} = 1$ chosen such that the H_2O-saturated solidus is seen at the highest temperature of the diagram. The point at which $M_{H2O} = 0$ consists of 1.03 Na_2O, 0.70 CaO, 2.58 K_2O, 6.68 FeO, 2.23 MgO, 16.42 Al_2O_3, 70.36 SiO_2, and 0 H_2O, whereas at $M_{H2O} = 1$, the composition is 0.91 Na_2O, 0.62 CaO, 2.28 K_2O, 5.91 FeO, 1.97 MgO, 14.51 Al_2O_3, 62.20 SiO_2, and 11.60 H_2O mole %. The value M_{H2O} = 0.22 corresponds to the H_2O content of the pseudosections in Figure 1, *etc*. The contours are for a_{H2O}. (In THERMOCALC, a_{H2O} is calculated *via* the datafile script "calcah2o").

reaction is the one corresponding to that in Figure 5 (*i.e.*, at fixed M_{H2O}): bi = g + cd + ksp + liq. In the first case, H_2O is provided from the system's environment to balance the reaction; in the second, the reaction is balanced for H_2O.

It is clear that using this T–a_{H2O} pseudosection when, in fact, systems being considered are closed and are operating at constant M_{H2O}, makes this figure diffcult to read without the benefit of Figure 5. For example, it is not obvious that such a wide range of starting positions at low temperature on this figure will all focus through the bi = g + cd + ksp + liq divariant reaction. However, on Figure 5, this fact is obvious, as this divariant field extends across the part of the figure of interest. Whereas the applicability of Figure 5 is obvious, such diagrams having been used to considerable effect, for example, by White *et al.* (2001) and by White & Powell (2002), it is less clear where Figure 6 will be directly applicable.

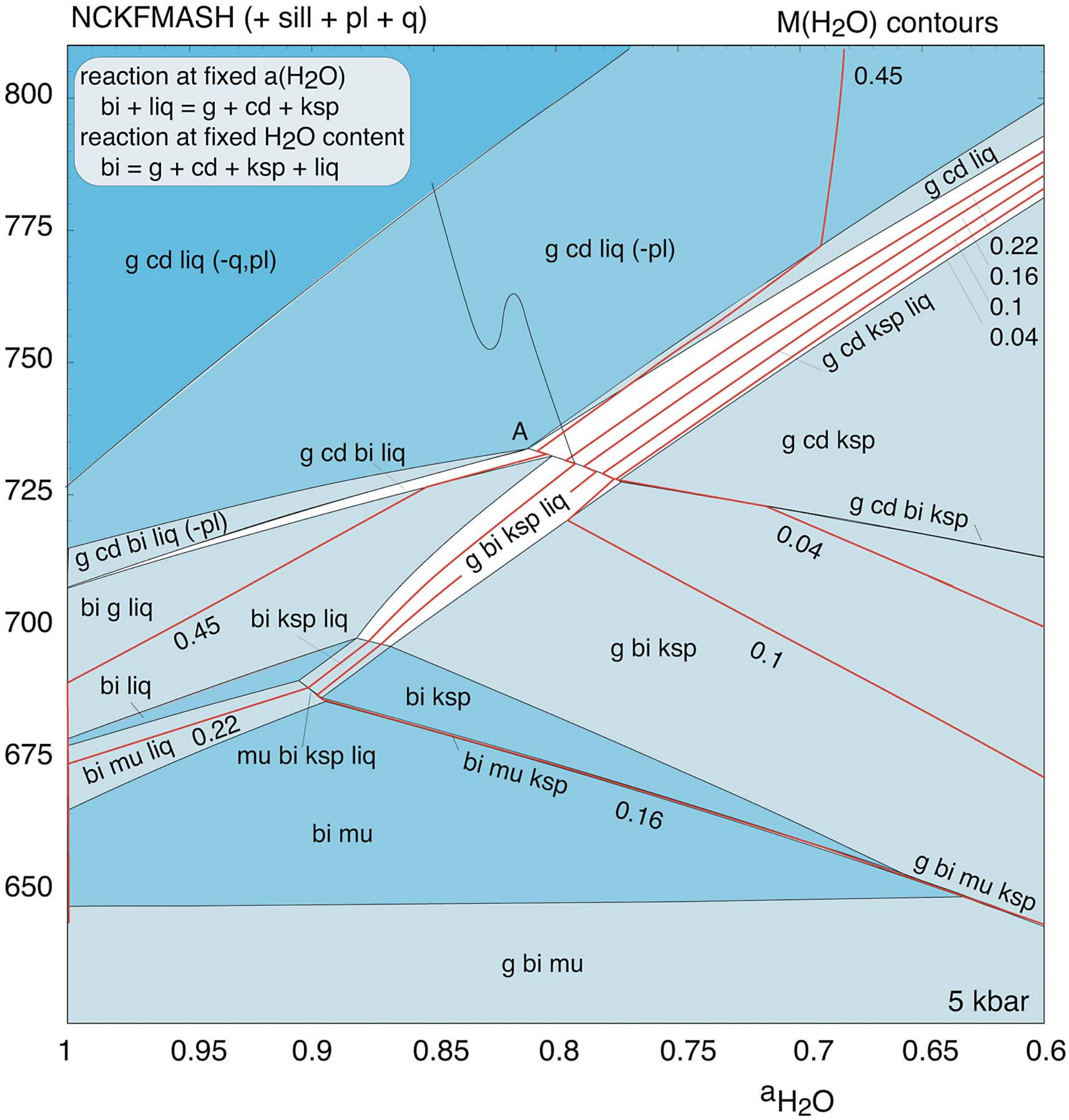


FIG. 6. The T–a_{H2O} pseudosection corresponding to Figure 5, for the bulk composition 1.03 Na_2O, 0.70 CaO, 2.58 K_2O, 6.68 FeO, 2.23 MgO, 16.42 Al_2O_3, 70.36 SiO_2 mole % (*i.e.*, the one for M_{H2O} = 0), with a_{H2O} varying. The contours are for the M_{H2O} values marked by arrows along the x axis of Figure 5.

However, if a rock for which Figure 6 is appropriate is adjacent to another rock with which it diffusively interacts, thus superimposing its a_{H2O} on it, the expected changes in mineral assemblage changes can be deduced using Figure 6. Although it is not wrong to talk about the variation of a_{H2O} during metamorphism (where a free fluid is not involved), these variations are not usually of interest in themselves if metamorphism is taking place at constant H_2O content.

Considering other "composition" variables, O_2 is one for which it has been commonplace to consider a_{O2} or, conventionally, but inaccurately, f_{O2}. This latter variable is almost never the controlling variable, the amount of Fe_2O_3 is. Calculations to consider relative oxidation of assemblages of metamorphic minerals are much more usefully done by varying Fe_2O_3 content rather than considering a_{O2} directly (White *et al.* 2000, 2002).

Conclusions

There is beauty and – with care! – truth in metamorphic mineral equilibria, but a sensible choice of which variables to put on the axes of phase diagrams makes the metamorphic geologist's job easier. Phase diagrams are potentially a more powerful tool for understanding metamorphic processes than those commonly employed (*i.e.*, *P–T*, *T–X*, and *P–X*) if the full range of variables is considered.

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