

A general thermodynamic analysis and treatment of phases and components in the analysis of phase assemblages in multicomponent systems

HU JiaWen^{1,2*}

¹ College of Resources, Shijiazhuang University of Economics, Shijiazhuang 050031, China;

² State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China

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Systematic thermodynamic analysis reveals that an essential condition for the thermodynamically valid chemographic projections proposed by Greenwood is completely excessive. In other words, the phases or components from which the projection is made need not be pure, nor have their chemical potentials fixed over the whole chemographic diagram. To facilitate the analysis of phase assemblages in multicomponent systems, all phases and components in the system are divided into internal and external ones in terms of their thermodynamic features and roles, where the external phases are those common to all assemblages in the system, and the external components include excess components and the components whose chemical potentials (or relevant intensive properties of components) are used to define the thermodynamic conditions of the system. This general classification overcomes the difficulties and defects in the previous classifications, and is easier to use than the previous ones. According to the above classification, the phase rule is transformed into a new form. This leads to two findings: (1) the degree of freedom of the system under the given conditions is only determined by the internal components and phases; (2) different external phases can be identified conveniently according to the conditions of the system before knowing the real phase relations. Based on the above results, a simple but general approach is proposed for the treatment of phases and components: all external phases and components can be eliminated from the system without affecting the phase relations, where the external components can be eliminated by appropriate chemographic projections. The projections have no restriction on the states of the phases or the chemical potentials of components from which the projections are made. The present work can give a unified explanation of the previous treatments of phases and components in the analysis of phase assemblages under various specific conditions. It helps to avoid potential misunderstandings or errors in the topological analysis of phase relations.

chemographic projection, compatibility diagram, phase rule, excess component, excess phase

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In the analysis of phase assemblages, the relationship between coexisting phases is often depicted with compatibility diagrams. In principle, a d -dimensional compatibility diagram can only display the phase relations of an $(d+1)$ -component system. Because of the limitation of the dimen-

sions of visual space, the dimensions of compatibility diagrams are very limited ($d \leq 3$). Therefore, for a system containing five or more components, we have to use chemographic projections, as was done by Korzhinskii [1] and Thompson [2]. For example, the assemblages including both quartz and muscovite in the $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-FeO-K}_2\text{O-H}_2\text{O}$ system open to H_2O were compositionally projected from H_2O , quartz, and muscovite onto the AFM

*Corresponding author (email: hu_jiawen@sina.com)

($\text{Al}_2\text{O}_3\text{-FeO-MgO}$) plane [2]. In this way, the paragenetic relations between minerals can be expressed and analyzed in a lower dimension composition space. In this projection, both quartz and muscovite are in excess, whereas H_2O is present in an unspecified state. Nevertheless, it is certain that the chemical potential or (fugacity, activity) of H_2O is a controlling factor of mineral assemblages. Compared with the projections from quartz and muscovite, the projection from H_2O may have a very different thermodynamic basis. As pointed out by Thompson [2], “the graphical analysis of mineral assemblages neglecting the amount of H_2O relative to other components seems to work. This is consistent either with the presence of pure water as a phase at the time the assemblage formed, or with the assemblage having reached its final state in accord with some externally controlled humidity.”

In the past decades, chemographic projections proved to be a very useful theoretical tool for the analysis of phase relations in multicomponent systems, and have been widely used in mineralogy, petrology, geochemistry, and chemical engineering. However, there is neither theoretically strict explanation for the legality of the various projections nor a general approach to guiding the treatments of components and phases in various chemographic projections. Therefore, there are still many theoretical problems to be solved in the analysis of phase assemblages.

(i) Misunderstandings on the legality, or validity, of chemographic projections. For example, in the extension of AFM projection to multicomponent system, Greenwood [3] proposed a condition for a thermodynamically “legal” (or valid) chemographic projections: if a chemographic diagram is a legal projection, then the phases or components from which the projection is made must either exist in pure state or have their chemical potentials fixed at a constant value over the entire diagram; otherwise, the projection will be thermodynamically illegal. However, as will be mentioned later, many chemographic projections do not satisfy the above condition. In these cases, the component from which the projection was made may be present in a mixture, or may have a variable chemical potential, or may have both features. Such projections are widely used as a common sense in chemical engineering, but no one has doubts about their legality. This suggests that the Greenwood’s projection condition must be revised; otherwise, a legal projection may be considered to be illegal [4], or may lead to other explanations [5].

(ii) The basis of the classification of components. Numerous chemographic projections suggest that the correct treatment of phases and components in the analysis of phase assemblages must be based on a correct analysis of the thermodynamic features and roles of all phases and components under consideration. The results of such an analysis can be summarized by a proper classification of both components and phases in terms of their thermodynamic features and roles under the given conditions. So far, there is not yet a

systematic or complete classification of phases for this purpose. Nevertheless, several classifications of components have been proposed for petrological systems [1, 6–8] (Appendix 1). In these classifications, the definitions of components are closely related to the feature whether the chemical potentials of components are environmentally controlled. In many cases, this feature disables the identification of components, because it is often very difficult to determine whether the system is open or closed, or whether the chemical potential of a component is relevant to the immediate surroundings (Appendix 1). After a systematic review, Rumble [9] concluded that the previous classifications of components have great difficulties in the discrimination of components when applied to petrological systems. Although these problems are very common in petrology, they are not handled well so as to leave much room for unexpected contradictions, misunderstandings, ambiguities, and errors [6, 8–13]. In fact, whether the chemical potentials of components are environmentally controlled is irrelevant to (or not important for) the topological analysis of phase relations. This fact makes it possible to present a better classification of components that can avoid the defects of past classifications.

(iii) A general theory or approach for various treatments of components and phases. In the analysis of phase assemblages, the treatments of components and phases were all conducted for the systems under specific conditions. In view of the diversity of systems and their thermodynamic conditions, it would be more desirable to develop a general theory or approach that can be used to treat many different systems, rather than to find a specific approach for every kind of them. Such a theory or approach should be more reliable and useful than the methods based on experiences, or specific conditions, particularly when meeting with completely unfamiliar systems or phase diagrams. It is important not only for explaining or justifying various approaches proposed for specific conditions and problems but also for avoiding potential errors or misunderstandings.

The principal purpose of this work is to present a simple but general approach for treatment of all components and phases on the basis of a general classification of components and phases. Meanwhile, some misunderstandings associated with thermodynamically valid chemographic projections are also corrected in this work.

1 Analysis of the components from which chemographic projections are made

The projection condition of Greenwood [3] is inconsistent with many thermodynamically valid projections, so it is actually an excessive constraint. In fact, in many cases, the components from which the projections are made are often present in mixtures, and their chemical potentials (μ_i) often vary with the thermodynamic conditions of systems, i.e.

temperature (T), pressure (P), and many properties of components, such as activity (a_i), fugacity (f_i), partial pressure (P_i), pH value, mass fraction (w_i), the amount of substance fraction (mole fraction, x_i), the amount of substance concentration (c_i), molality (m_i), etc., where i is a component. Here are some typical examples.

(i) P - T phase diagrams with excess phase(s) [4, 14–31]. The phase assemblages in these phase diagrams can be depicted in the projection of phase composition space from excess components, where the chemical potentials of excess components are not fixed, but vary with the P - T conditions (and therefore vary with phase assemblage). In some of these phase diagrams [25–27], the excess phases include a melt (a H_2O -bearing liquid).

(ii) P - X_i or T - X_i diagrams with or without excess phase(s), where X_i is a property of component i , such as μ_i , a_i , f_i , P_i , pH value, x_i , w_i , m_i , c_i , etc. [14, 28, 31–36]. The phase assemblages in these diagrams can be displayed in the chemographic projections from component i and properly chosen excess component(s) (if any) (e.g. Figures 1 and 2) [14, 32–35]. Similarly, μ_i may vary with the thermodynamic conditions of divariant or univariant assemblages. Additionally, in some phase diagrams of this type, the component i may be in an impure state, such as many isothermal P - $x(CO_2)$ diagrams or isobaric T - $x(CO_2)$ diagrams in the presence of CO_2 - H_2O fluid [28, 32, 37]. For these diagrams, the chemographic diagrams can be obtained from projections from CO_2 and H_2O (Figure 1), and we have no reasons to doubt their validity or legality.

(iii) Chemical potential (or activity, fugacity) diagrams [33, 34, 37–41]. For example, in Figure 3, the chemographic diagram is obtained by projections of phase composition space from CO_2 , H_2O , CaO , Na_2O , and K_2O , respectively. Although $\mu(CO_2)$, $\mu(H_2O)$ and $\mu(CaO)$ are constant, but $\mu(Na_2O)$ and $\mu(K_2O)$ are variable in all divariant regions. Furthermore, Na_2O and K_2O are unlikely to be present as pure substances in the metasomatic process.

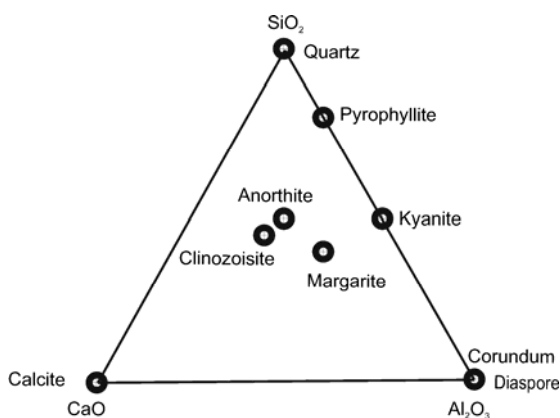


Figure 1 Chemographic diagram for the T - $x(CO_2)$ diagram of the system CaO - SiO_2 - Al_2O_3 - CO_2 - H_2O at 5 kbar (projected from CO_2 and H_2O , after Ranson [32]).

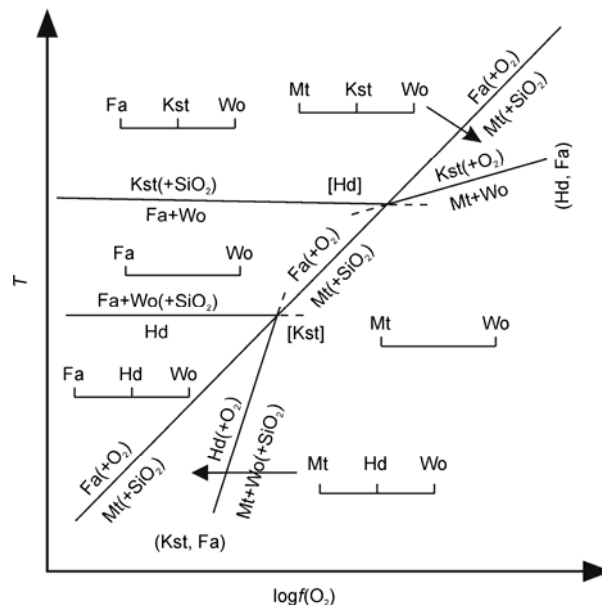


Figure 2 The T - $\log f(O_2)$ diagram of the Fe - Ca - Si - O system at fixed P and $a(SiO_2)$.

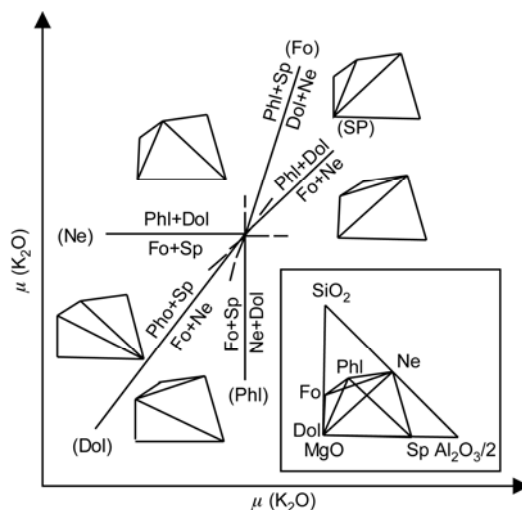


Figure 3 The $\mu(K_2O)$ - $\mu(Na_2O)$ diagram of some minerals coexisting with calcite in the metasomatic lazurite deposits in the southern Pribaikal'e, Russia (after Figure 75 of Korzhinskii [1]). The values of P , T and $\mu(CO_2)$ and $\mu(H_2O)$ are assumed to be constant. The ubiquitous presence of calcite indicates that $\mu(CaO)$ should be also constant. Dol, dolomite; Sp, spinel; Ne, nepheline; Phl, phlogopite; Fo, forsterite.

(iv) The dry-salt solubility diagram of salt-water systems at constant T and P . Take Figure 4 as example. This is a projection of solution saturation surface from H_2O and MgB_4O_7 on the Na - K - SO_4 plane. In this system, the solution and $MgB_4O_7 \cdot 9H_2O$ crystal are excess phases, and H_2O and MgB_4O_7 are their excess components, respectively. It is apparent that the excess H_2O here is present in a solution, not pure water. Furthermore, $\mu(H_2O)$ is not fixed, but varies in all divariant regions. Such projections are widely used in chemistry and chemical engineering [43–46].

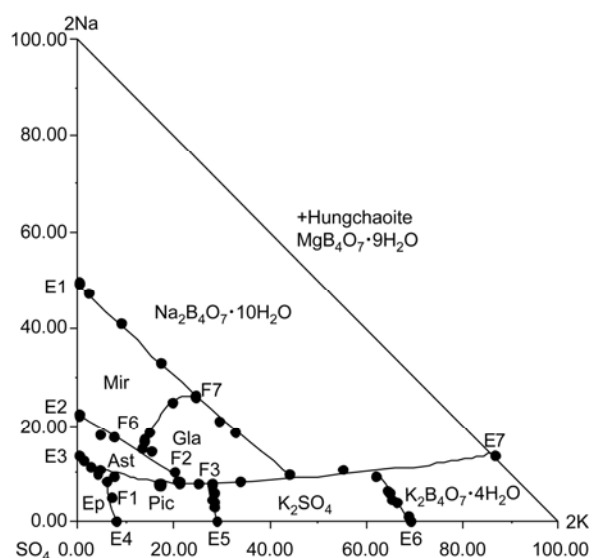


Figure 4 The solubility diagram of the Na-K-Mg-SO₄-B₄O₇-H₂O system at 288 K and 101 kPa [42]. This is a projection of the solution saturation surface from H₂O and MgB₄O₇, where hungchaoite (MgB₄O₇·9H₂O) exists in all assemblages; E1–E7 and F1–F7 are invariant points. The dots are experimental results. Ep, Epsomite (MgSO₄·7H₂O); Mir, mirabilite (Na₂SO₄·10H₂O); Pic, picromite (K₂SO₄·MgSO₄·6H₂O); Ast, astrakhanite (Na₂SO₄·MgSO₄·4H₂O); Gla, glaserite (Na₂SO₄·3K₂SO₄).

In fact, a component present as pure phase with a fixed chemical potential is only a limiting case of the numerous impure states under natural conditions. For instance, pure H₂O is simply a limiting case of excess H₂O in solutions or gaseous mixtures [2, 47], because the prevailing state of H₂O in most natural environments is $a(\text{H}_2\text{O}) < 1$, which can be viewed as a hypothetical (impure) form of H₂O [2]. On the other hand, excess H₂O present as a solution does not alter the basic features of phase diagram topology [7], because any other extraneous component not present as an independent phase does not change the calculated result of phase rule [48]. This conclusion also applies to the numerous excess melts, solid solutions, or fluid mixtures.

For an excess phase, it is either pure or impure. In the first case, the excess phase is either one-component substance (namely pure excess component), such as the quartz in AFM projection, or a multicomponent compound, such as the calcite in Figure 3 and the MgB₄O₇·9H₂O crystal in Figure 4. In the second case, it is a mixture of an excess component and other component(s), such as the aqueous solution in Figure 4 and the melts in *P-T* phase diagrams [4, 25–27]. In many systems, an excess component can exist in more than one phase. For example, in Figure 4, the excess component MgB₄O₇ is present in both solution and MgB₄O₇·9H₂O, and the excess component H₂O is present in the solution and most solid phases in Figure 4 (such as MgB₄O₇·9H₂O, MgSO₄·7H₂O, Na₂SO₄·10H₂O, K₂SO₄·MgSO₄·6H₂O, and Na₂SO₄·MgSO₄·4H₂O). In the AFM projection, the excess SiO₂ can be found in quartz, musco-

vite, and other minerals. Despite this fact, any excess component can only form one excess phase at given conditions and the fundamental factor for the formation of an excess phase should be the sufficient content (or concentration, activity, etc.) of a specified component. For example, excess pure water can be viewed as a limiting case in which $\mu(\text{H}_2\text{O})$ reaches its maximum value [47]. On the other hand, no one has found such system where two or more excess components form only one excess phase at given conditions. In other words, there is a one-to-one correspondence between excess components and excess phases:

$$c_{\text{ex}} = p_{\text{ex}}, \quad (1)$$

where c_{ex} and p_{ex} are the numbers of excess components and excess phases, respectively. The correctness of this relation has been verified by numerous systems. It is worth noting that eq. (1) does not have any restriction on the chemical potentials of excess components, or the states of excess phases. That is, the chemical potential of an excess component can be fixed, or variable, and an excess phase can be present in solid, liquid, gas or supercritical state [1, 2, 19, 49, 50].

Generally, a divariant assemblage exists in a divariant region (rather than on a point in it), where the chemical potential of the component from which chemographic projection is made can be either *fixed* or *variable* depending on the properties of the system or phase diagram. In most cases, the chemical potentials of the excess components are variable, e.g., pure excess phase(s) at variable *P* and/or *T* [18, 23], or excess fluid mixture(s) of variable composition [50], or excess melts [4, 26, 27] in multicomponent systems at variable *P* and/or *T*.

For a divariant (or univariant, invariant) assemblage in a legal compatibility diagram obtained by projections from components 1, 2, ..., and *k*, all coexisting phases must have the same *P*, *T*, μ_1 , μ_2 , ..., and μ_k at a specified equilibrium state. However, since the stability field of a divariant assemblage is a divariant region, μ_1 , μ_2 , ..., and μ_k can vary from one equilibrium state to another in the divariant region, or vary from one assemblage to another. Of course, in some special cases, μ_i , μ_j , ..., and μ_k (or a part of them) do keep constant in all assemblages, such as the chemical potential of the excess component in an excess phase of fixed composition at fixed *P* and *T*.

2 A general classification and treatment of components

2.1 Classification of components

In addition to *P* and *T* (fixed or variable), the condition parameters of the systems or phase diagrams in question often include the following properties of components:

(i) Independent variables μ_i , a_i , f_i , P_i , x_i , w_i , m_i , c_i , pH value, etc. For example, in the isothermal P - $x(\text{CO}_2)$ phase diagram of the $\text{MgO-SiO}_2\text{-CO}_2\text{-H}_2\text{O}$ system, $x(\text{CO}_2)$ is a condition variable of the stabilities of all phase assemblages at the given T . So are the coordinate variables $\mu(\text{K}_2\text{O})$, $\mu(\text{Na}_2\text{O})$ in Figure 3, the Jänecke indices in Figure 4, and the compositional variables in Figures 5 and 6.

(ii) Constrained variables μ_i , a_i , f_i , P_i , x_i , w_i , m_i , c_i , pH value, etc. They are either fixed, or variable but subject to a constraint, such as the P - T pseudosection of the $\text{MgO-SiO}_2\text{-CO}_2\text{-H}_2\text{O}$ system at given $x(\text{CO}_2)$, where the given $x(\text{CO}_2)$ is a constraint condition of all phase assemblages in the pseudosection. Similarly, in the P - T pseudosections at given $x(\text{Mg})$ [25, 51, 52], or the P - T sections at given $a(\text{H}_2\text{O})$ [53–56], the T - $m(\text{H}_4\text{SiO}_4)$ and T - $a(\text{Al}_2\text{O}_3)$

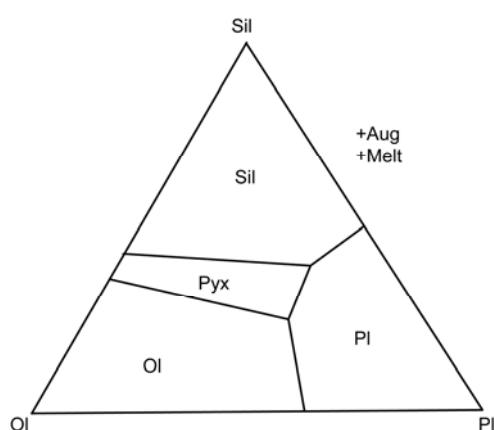


Figure 5 Projection of low-pressure silicate liquidus surface from Ca-SiO_3 in the pseudo-quaternary system wollastonite-olivine-plagioclase-quartz (taken from Figure 2 of Longhi [5]). Ol, Olivine; Pl, plagioclase; Sil, silica phase (tridymite or cristobalite); Pyx, low-Ca pyroxene; Aug, augite.

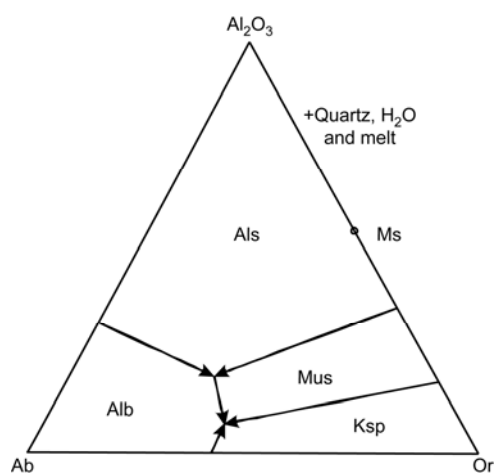


Figure 6 Possible liquidus diagram for the quartz and H_2O -saturated portion of the system $\text{AlO}_2\text{-NaAlO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ (KNASH) at some fixed pressure (Taken from Thompson and Algor [18]). Ab, $\text{NaAlSi}_3\text{O}_8$; Or, KAlSi_3O_8 ; Ms, $\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$; Alb, sodic alkali feldspar; Ksp, potassic alkali feldspar; Als, Al_2SiO_5 (kyanite, sillimanite, or andalusite); Mus, potassic white mica. The arrows stand for the directions of falling cotectic temperatures.

sections at given $a(\text{Beryl})$ [57], or the T - $\log f(\text{O}_2)$ section at given $a(\text{SiO}_2)$ (Figure 2) [58], where the given “composition, concentration” or activity is a constraint condition of the phase assemblages in its corresponding phase diagram.

On the other hand, there are often such instances that the system has one or more phases common to all phase assemblages. The existence of every common phase is essentially a constraint condition of all phase assemblages under consideration, which reduces one degree of freedom of the system. Based on the difference in their thermodynamic features and roles, common phases can be divided into two subgroups:

(i) Excess phase(s). For any excess phase, there is always a component responsible for its presence. This is the so-called excess component, whose amount or concentration (or activity, fugacity) is enough for the formation of an independent phase present in excess. Excess components may be present as pure substances or mixtures, such as the excess H_2O in pure water (solid, liquid, gas or supercritical state), aqueous solutions, gaseous mixtures or supercritical fluid mixtures. Excess components can directly influence the stabilities of excess phases and any other phase(s) containing them. Besides, if an excess phase is a mixture, its excess component can also directly interact with coexisting components, whose chemical potentials further influence the stabilities of other phases (e.g. Figure 4).

(ii) Non-excess common phase(s). Unlike excess phase(s), the presence of such a phase in all assemblages is not due to the high content (or concentration, activity, fugacity, etc.) of a specified component, but due to the appropriate P or T at which this phase can exist in equilibrium with other phases in the system, where the P or T can vary from one state to another, but is not used as a coordinate of the phase diagram (namely an independent condition variable of the system). Take for example, the liquidus composition diagram in Figures 5 and 6, which are the projections of solid-melt saturation surfaces from the higher temperature side on their corresponding composition planes, because a melt is only stable at the higher temperature side of solid-melt saturation surface. In this diagram, every point corresponds to a solid-melt equilibrium temperature at the given pressure, so the equilibrium temperature varies from point to point. In other words, the diagram implicitly contains a variable temperature, although it is not an independent variable. These features are common to all isobaric liquidus diagrams [18, 50, 59–67]. On the other hand, the melting processes of solids are almost always (except for ice) accompanied by an increase in volume. That is, a liquidus composition diagram can also be obtained by projection of an isothermal solid-melt saturation surface from the lower pressure side on composition plane. In fact, the non-excess common phases that are most frequently met in mineralogy and petrology are the melts in various isobaric liquidus diagrams. Besides, non-excess common phases may be present in other states (either pure or impure), such as the fluid in

Figure 7, which implicitly contains a non-independent temperature variable, and every point in it defines a chemical equilibrium temperature. In brief, if a phase diagram includes a non-excess common phase k , it can be regarded as being obtained by projecting the equilibrium surface of the assemblages containing phase k along the direction of P or T . The resulting phase diagram (or its corresponding system) must *implicitly* include a non-independent temperature or pressure variable, which varies from point to point (or from one state to another). This feature can be used to discriminate the existence of non-excess common phases.

In essence, the properties of components and common phases used to define the thermodynamic conditions of a system or a phase diagram are the condition variables or constraint conditions that are external to the other phases and components. For this reason, the phases and components used to define the thermodynamic conditions are defined as external phases and external components, respectively. Accordingly, the other phases and components are internal phases and internal components, respectively.

By definition, internal phases are only stable in some (not all) of the phase assemblages in the system, whereas external phases are all common phases, i.e. excess phases and non-excess common phases. The external components can also be divided into two subgroups: (1) excess components; (2) the other external components, namely, the components whose chemical potentials (or relevant properties, e.g. compositions, concentrations, activities, fugacities, etc.) are directly used to define the constraint conditions or coordinates of phase diagrams (namely condition variables of the systems). For this reason, the components in this subgroup can be defined simply as “condition” components. The above classification is summarized in Table 1.

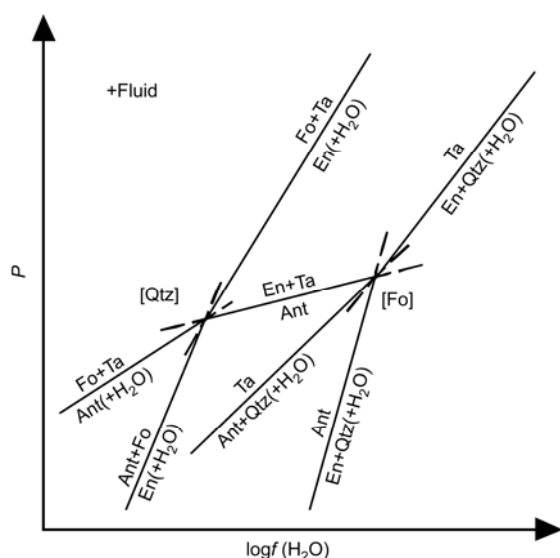


Figure 7 Schematic projection of fluid-bearing equilibrium surface of the MgO-SiO₂-H₂O system from the higher temperature side on the P - $\log f(\text{H}_2\text{O})$ plane (Plotted after calculated P - T phase diagram of the MgO-SiO₂-H₂O system [68]). Ant, Anthophyllite; En, enstatite; Fo, forsterite; Ta, talc; Qtz, quartz.

Table 1 Classification of phases and components

Object	Group	Subgroup
Phases	External phases	Excess phases Non-excess common phase(s)
	Internal phases	
Components	External components	Excess components Condition components
	Internal components	

The above classification overcomes the deficiencies and difficulties in previous classifications. In this work, all phases and components needing different treatments in the topological analysis of phase relations are defined unambiguously. In particular, the definition of external components is irrelevant to the chemical potentials of components or their influencing factors, so all external components can be determined very easily. For example, in the P - T diagram of the MgO-FeO-SiO₂-CO₂-H₂O system at fixed $x(\text{CO}_2)$, the fixed $x(\text{CO}_2)$ is an influencing factor external to the investigated mineral assemblages, so CO₂ is a condition component. The fixed $x(\text{CO}_2)$ also indicates that the fluid (CO₂-H₂O mixture) is present in excess. Since CO₂ is a condition component, the excess component must be H₂O. In this situation, both H₂O and CO₂ are external components. The other components are all internal components.

2.2 Reformulation of the phase rule

In most cases, the influence of interfacial tensions and outer fields (such as electric, magnetic and gravity field) on the system can be neglected. Under this convention, the degree of freedom of the system (f) can be described with extended Gibbs phase rule:

$$f = c - p + 2 - r, \quad (2)$$

where p and c are the numbers of phases and independent components in the system, respectively, and r is the number of independent constraints on intensive variables, except for the independent constraints on compositions, concentrations, or partial pressures that arise from all stoichiometric relations (including charge balance conditions), because these constraints have been counted in the definition of c [69].

According to the classification in this work, p and c can be rewritten as

$$p = p_{\text{ex}} + p_{\text{nc}} + p_{\text{in}}, \quad (3)$$

$$c = c_{\text{ex}} + c_{\text{cn}} + c_{\text{in}}, \quad (4)$$

where c_{ex} , c_{cn} and c_{in} are the numbers of excess components, condition components and internal components, respectively; p_{ex} , p_{nc} , and p_{in} are the numbers of excess phases, non-excess common phases, and internal phases, respectively. With eqs. (3), (4) and (1), eq. (2) can be rewritten as

$$f = c_{\text{in}} - p_{\text{in}} + 2 + (c_{\text{cn}} - p_{\text{nc}} - r). \quad (5)$$

For 2-dimensional phase diagrams, the bracketed terms are always zero, that is,

$$f = c_{\text{in}} - p_{\text{in}} + 2, \quad (6)$$

$$c_{\text{cn}} - p_{\text{nc}} - r = 0. \quad (7)$$

Eqs. (6) and (7) are also valid for the systems with two independent condition variables, where the phase relations can be described in 2-dimensional phase diagrams (i.e. $f = 0-2$). This finding has been tested with numerous representative real systems and phase diagrams.

For d -dimensional phase diagrams or the systems with d independent condition variables (i.e. $f = 0-d$), eqs. (6) and (7) can be generalized as

$$f = c_{\text{in}} - p_{\text{in}} + d, \quad (8)$$

$$c_{\text{cn}} - p_{\text{nc}} - r = d - 2, \quad (9)$$

where c_{in} and p_{in} can be obtained from simple transformations of eqs. (3) and (4):

$$p_{\text{in}} = P - p_{\text{ex}} - p_{\text{nc}}. \quad (10)$$

$$c_{\text{in}} = c - c_{\text{cn}} - c_{\text{ex}}. \quad (11)$$

Eq. (9) is an important relation, where c_{cn} , r , and d are only determined by the conditions of the system. It is very interesting that eq. (9) can be reformulated as a form similar to eq. (2), i.e. $d = c_{\text{cn}} - p_{\text{nc}} + 2 - r$. Besides, eq. (9) can also be used to determine the value of p_{nc} :

$$p_{\text{nc}} = c_{\text{cn}} - r - (d - 2). \quad (12)$$

If $p_{\text{nc}} > 0$, it will indicate that the system has p_{nc} non-excess common phases; if $p_{\text{nc}} = 0$, there will be no non-excess common phase, i.e. the system only contains internal phases, or excess phases and internal phases. Apparently, if $d = 2$, eq. (12) will degenerate into $p_{\text{nc}} = c_{\text{cn}} - r$. Eq. (12) can be used to distinguish excess phases from non-excess common phases. For example, if a system has some phase(s) common to all phase assemblages, at the same time the calculated $p_{\text{nc}} = 0$, then the common phase(s) must be excess phase(s). Eqs. (1) and (12) clearly reveal the difference between excess phases and non-excess common phases: the existence of an excess phase counteracts the contribution of its corresponding excess component to f , whereas the existence of a non-excess common phase counteracts the contribution of a condition component whose chemical potential (or relevant property) is a coordinate variable. The latter relation is evident when $r = 0$ and $d = 2$.

2.3 Treatment of components

As analyzed above, external phases and components are essentially external controlling factors of all phase assem-

blages of interest, so they need not appear in the chemographic diagram or compatibility diagrams of the system. In other words, they can be ignored in the analysis of phase assemblages without affecting the correctness of results. At the same time, they can also be treated in a unified way:

(i) Condition components can be eliminated by projecting the phase composition space from their composition points onto a subspace without the points, such as CO_2 in Figure 1, O_2 in Figure 2, and CO_2 , H_2O , Na_2O and K_2O in Figure 3.

(ii) Non-excess common phases can be directly ignored, such as the melts in Figures 5 and 6, and the fluid in Figure 7.

(iii) Excess components and excess phases can be eliminated together by projecting the phase composition space from appropriate points onto a subspace without the points. As can be seen here, excess phases and non-excess common phases are treated in very different ways.

In the above projections, an excess component may have the same composition as its corresponding excess phase. In this case, the projection is also thought to be made from the excess phase, such as the projection from quartz in AFM projection. In other cases, an excess component may be only a simple component in its corresponding excess phase, such as CaO in calcite in Figure 3 and the H_2O in aqueous solution in Figure 4. An excess component can also be a linear combination of two or more simple components, such as the component MgB_4O_7 ($\text{MgO} + 2\text{B}_2\text{O}_3$) in hungchaoite (Figure 4), and the component KAl_3O_5 ($0.5\text{K}_2\text{O} + 1.5\text{Al}_2\text{O}_3$) in muscovite in AFM projection [2]. Moreover, even a melt can serve as an excess component [70]. Like excess components, a condition component may be a simple component, or a linear combination of two or more simple components, and sometimes the combinatorial coefficients can be negative [71], such as $\text{F}_2\text{-O}$ [39], $\text{K}^+ - \text{H}^+$ [72], $\text{H}_2\text{O} - \text{H}_2$, $\text{Fe}^{2+} - \text{Ca}^{2+}$ [73], $\text{Al}^{3+} - 3\text{H}^+$, $\text{Ca}^{3+} - 2\text{H}^+$ [74, 75]. Now, the theories and approaches for chemographic projections have covered a variety of systems [1-3, 16, 26, 27, 37, 39, 54, 59, 70, 71, 76-80]. The details on this topic will not be repeated here.

The above projections have no restriction on the states or the chemical potentials of the components from which the projections are made. The direct result of the projection(s) is a chemographic diagram, which can be used to construct compatibility diagrams. After the above treatments, the resulting chemographic diagram only contains internal components and phases. These components and phases form a hypothetical model system that is essentially equivalent to the real system in phase relations. For 2-dimensional phase diagrams (or equivalent systems with two independent intensive variables), the resulting model systems obey the Gibbs phase rule. In this case, the phase relations can be analyzed like those in typical P - T phase diagrams. As a result, the theory for the topological analysis of phase diagrams based on Schreinemakers' rules and their various extensions [81-84] can be directly applied to the model

system. This, of course, will greatly extend the applicable range of phase diagram topology.

3 Correction of some misunderstandings

3.1 Chemographic projections

In mineralogical and petrological research, there are some very typical misunderstandings on the legality of chemographic projections. For example, in analyzing the paragenetic relationship between minerals in the quartz-bearing metapelites from Brattstrand Bluffs, Fitzsimons [4] used an AFM diagram ($A=Al_2O_3-K_2O-Na_2O-CaO$), which was obtained by projection from quartz, K-feldspar, and H_2O . According to Fitzsimons [4], the volatile-undersaturated melts and their coexisting H_2O -bearing minerals would have buffered $\mu(H_2O)$, but their H_2O content, and therefore $\mu(H_2O)$, must have varied significantly during the partial melting and melt crystallization. On the other hand, the spinel, garnet and cordierite compositions are consistent with equilibrium over a restricted range of P - T - $\mu(H_2O)$, so the phases did not all coexist at fixed $\mu(H_2O)$. For this reason, the AFM diagram was thought to be invalid [4]. In fact, as revealed in the previous section, whether $\mu(H_2O)$ was fixed is not important for the projection. In this example, the problems to be made clear are whether the melts and their coexisting minerals really attained thermodynamic equilibria, and whether quartz and K-feldspar were really present in excess. If so, the AFM diagram should be valid.

In the modeling of fractional and equilibrium crystallization of natural basaltic liquids, Longhi [5] employed a projection of the low-pressure liquidus surface of the pseudo-quaternary system OI-Pl-Wo-Qtz (Olivine-Plagioclase-Wollastonite-Quartz) from Wo ($CaSiO_3$) onto the OI-Pl-Qtz plane (Figure 5). This projection results in an augite-excess liquidus plane. Given that the mineral Wo is never present as a saturating phase and is rarely observed in basaltic rocks, the projection was thought to be optical, rather than thermodynamic [5]. In fact, if all assemblages under consideration really reached their stable equilibrium states, the projection should be legal, because the excess component ($CaSiO_3$) from which the projection is made need not be present as a saturating phase (Wo), i.e. an excess phase can be a homogeneous mixture containing both excess component and other ones. In this example, Wo only serve as an excess component, not an excess phase. The relationship between Wo and augite here is essentially similar to that between H_2O and aqueous solution in the solubility diagrams of multicomponent salt-water systems at constant P and T .

3.2 Excess components

Sometimes, excess components may be confused with other

external components. Take the T - $x(CO_2)$ diagram of the $CaO-Al_2O_3-SiO_2-H_2O-CO_2$ system at $P = 500$ MPa as example, where P is equal to fluid pressure. In this system, both H_2O and CO_2 were considered to be excess [32]. However, according to the classification in this work, this understanding should be modified. Eq. (1) suggests that it is impossible for two excess components to form only one excess phase. In this example, CO_2 should be a condition component ($c_{cn} = 1$), because $x(CO_2)$ is a coordinate variable. Given that the total pressure completely comes from fluid, the fluid must be excess in the system, so $p_{ex} = 1$. Since CO_2 is a condition component, the excess component must be H_2O ($c_{ex} = 1$). For this reason, both CO_2 and H_2O should be excluded through compositional projection. The resulting chemographic diagram is a $CaO-SiO_2-Al_2O_3$ triangle, which is the same as that of Ranson [32], but the theoretical explanation is very different.

4 Analysis of AFM projection based on the present work

In the AFM projection, quartz and muscovite are ignored because they are excess phases. Accordingly, their corresponding excess components should also be excluded by compositional projections. The component H_2O was eliminated for a rather different reason [2, 47], i.e. H_2O is an external component, whose state is actually unspecified. As mentioned in the classification, an external component like H_2O in the AFM projection can be present in three kinds of states: (i) an unknown or hypothetical state with variable chemical potential (or fugacity, activity, concentration, etc.), (ii) an unknown or hypothetical state with constrained (including fixed) chemical potential; and (iii) excess phase, which may be pure water (solid, liquid, gas or supercritical fluid), or H_2O -bearing mixtures. The p_{nc} values in the three states can be determined unambiguously. For example, in the first state, $\mu(H_2O)$ is a controlling factor of the mineral assemblages, so H_2O is a condition component ($c_{cn} = 1$). If P , T and $\mu(H_2O)$ are all independent variables, then $r = 0$, $d = 3$, $p_{nc} = 1 - 0 - (3 - 2) = 0$. If there is a constraint on P or T (e.g. P or T is fixed), then $r = 1$, $d = 2$, $p_{nc} = 1 - 1 - (2 - 2) = 0$. In the second case, the constrained $\mu(H_2O)$ indicates that $r = 1$, $c_{cn} = 1$ (i.e. H_2O is a condition component). The independent variables P and T indicate $d = 2$, so $p_{nc} = c_{cn} - r - (d - 2) = 1 - 1 - (2 - 2) = 0$. In the third state, $c_{cn} = 0$, $r = 0$, $d = 2$, $p_{nc} = 1 - 0 - (2 - 2) = 0$. That is to say, there is no non-excess phase in the assemblages under consideration. These results are consistent with facts. The three cases above summarize various possibilities of H_2O as an external component in various geological settings. In any of the cases, H_2O can be ignored without affecting the representation of phase relations. Of course, in the third state, H_2O and its corresponding excess phase can be ignored together.

5 Analysis of phase assemblages in multicomponent phase diagrams

Take Figures 3 and 4 as examples. In Figure 3, CO_2 , H_2O , K_2O and Na_2O are all condition components ($c_{\text{cn}} = 4$), because $\mu(\text{CO}_2)$ and $\mu(\text{H}_2\text{O})$ are fixed condition parameters and $\mu(\text{K}_2\text{O})$ and $\mu(\text{Na}_2\text{O})$ are coordinate variables, i.e. the controlling variables of all mineral assemblages in question. The fixed P , T , $\mu(\text{CO}_2)$ and $\mu(\text{H}_2\text{O})$ indicate $r = 4$, so $p_{\text{nc}} = c_{\text{cn}} - r = 4 - 4 = 0$, i.e. there is no non-excess common phase. This suggests that the calcite is excess in the system. Since CO_2 is a condition component, the excess component in calcite must be CaO ($c_{\text{ex}} = p_{\text{ex}} = 1$). According to the general approach in this work, the condition components CO_2 , H_2O , K_2O and Na_2O can be eliminated by projections of the complete phase composition space from their composition points, respectively. The excess CaO and calcite can be eliminated together by further projection from the composition point of CaO . The final projection is a composition triangle ($\text{SiO}_2\text{-MgO-Al}_2\text{O}_3$). On this triangle, all divariant assemblages can be displayed and analyzed very clearly (Figure 3).

In Figure 4, there are three compositional variables, but only two of them are independent due to the constraint $x(\text{Na}) + x(\text{K}) + x(\text{SO}_4) = 1$. That is, Figure 4 has only two independent coordinate variables. Accordingly, there are only two condition components ($c_{\text{cn}} = 2$). The constant P and T indicates $r = 2$, so $p_{\text{nc}} = c_{\text{cn}} - r = 2 - 2 = 0$, i.e. there is no non-excess common phase. Therefore, the solution and $\text{MgB}_4\text{O}_7 \cdot 9\text{H}_2\text{O}$ must be excess phases, where H_2O and MgB_4O_7 are their corresponding excess components. Now, it is evident that the system has four external components (two condition components plus two excess components). There is only one internal component in the system ($c_{\text{in}} = c - c_{\text{cn}} - c_{\text{ex}} = 5 - 2 - 2 = 1$). That is, the model system is unary. This result can explain why Figure 4 only has three univariant lines about each invariant point (because $p_{\text{in}} = c_{\text{in}} + 2 = 3$ when $f = 0$).

In some cases, the chemographic projections from some condition components can also be omitted for practical purpose when the dimensions of phase composition space is already low enough for a clear representation of phase assemblages. For example, the projections from Na^+ and K^+ in Figure 4 can be omitted, because the phase composition space after projections from H_2O and MgB_4O_7 becomes a Na-K-SO_4 triangle. At this stage, further projections are completely unnecessary, because all phase assemblages in the system can be displayed and analyzed conveniently in the triangle, where the composition point of an internal phase defines a divariant assemblage, the tie-line connecting two specified internal phases defines a univariant assemblage, and a tie-line triangle defines an invariant assemblage. Similarly, the projections from Qtz and Pl (or any other pair

of components) in Figure 5 can also be omitted, because the projection of the phase composition space from CaSiO_3 (the excess component in augite) is an Ol-Pl-Qtz triangle, which is already enough for a clear representation of all assemblages.

6 Conclusions

It is demonstrated that that the condition for the thermodynamically valid chemographic projections proposed by Greenwood [3] is unnecessary. Some relevant misunderstandings are also corrected accordingly.

We also present a general classification of components and phases for the analysis of phase assemblages, where all phases and components needing different treatments are unambiguously classified and defined in terms of their different thermodynamic features and roles. The phases and components in question are divided into two groups: internal and external ones. This classification overcomes the difficulties and deficiencies in previous classifications, so it is more general and easier to use than previous ones. Particularly, all components and phases defined in this work can be determined very easily. According to the above classification, the phase rule is transformed into a new form similar to Gibbs phase rule. In this process, it is found that (1) the degree of freedom of the system under given conditions is only determined by the internal components and phases; (2) the non-excess common phases can be identified conveniently according to the conditions of the system, and can be distinguished strictly from excess phases without knowing the real phase relations.

The above results enable one to give a unified treatment of the phases and components: all external phases can be excluded from the system; all external components can be excluded from the phase composition space by appropriate chemographic projections. The projections have no restriction on the states of excess phases, or the chemical potentials of the components from which the projections are made. This is a significant generalization of thermodynamically valid projections. The present work allows us to give a unified explanation for the previous treatments of phases and components in various specific systems. It can serve as a useful and convenient tool for those who are unfamiliar with the analysis of phase assemblages in multicomponent systems.

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Appendix 1 Past classifications of components

In the thermodynamic analysis of paragenetic mineral assemblages, Korzhinskii [1] divided all components in a system into two groups: (1) the (perfectly) mobile components, whose chemical potentials or relevant intensive properties (e.g. activities, partial pressures, or concentrations in specific phases) are the influencing factors of equilibrium of the system; (2) inert components, whose masses or molar amounts (i.e., extensive properties) are independent variables (the influencing factors of equilibrium) of the system. The inert components include several subgroups: (1) trace components, (2) isomorphous components in a group of rocks with definite ranges of variation in contents, (3) accessory (indifferent) components, which either separate out in pure form or combine with (perfectly) mobile components but do not enter the rest coexisting phases, or do so in small amounts without affecting the paragenetic relations, (4) excess components, and (5) the determining inert components, namely, the inert components whose mutual relations determine the mineralogical composition of the paragenetic group. In fact, it is completely unnecessary to introduce dynamic factors like mobility of components into the topological analysis of phase diagrams. Owing to the relativity of motions, the concept of (perfectly) mobile component may give erroneous conclusions for the assemblages whose components are mobile [6]. The definitions of Korzhinskii [1] may lead to unexpected confusions or misunderstandings. For example, during the crystallization of a brine system induced by gradual isothermal evaporation of water, the gradually dropping mass of H₂O is an independent parameter of state of the system, so H₂O should be an inert component [1]. On the other hand, $\mu(\text{H}_2\text{O})$ also varies with the vaporization process, so H₂O must be also a (perfectly) mobile component. Now, the same component is both inert and mobile. In the paragenetic analysis of metasomatic minerals in the Archean phlogopite deposits (Figure 3), the components CO₂ and CaO in the excess calcite (CaCO₃) were considered to be perfectly mobile [1]. However, according to the classification of Korzhinskii, excess components should be inert components [1]. Again, the same component is both inert and mobile. The defects inherent in the classification above have led to divergent understandings [8], and thus received criticisms and discussions [6, 8, 10–13]. These facts may help to explain why Korzhinskii's classification is almost forgotten in recent years.

Thompson [6] defined several concepts for the components in the mineral assemblages in metasomatic rocks, such as actual, inactive, nonvariable, possible, ultimate and other components. Among them, there are two groups of components worthy of note: (1) ultimate components, which are sufficient and necessary for defining (or writing formulas for) all actual components in all phases in a given sequence of metasomatic assemblage. These components play

the roles of the independent components in the conventional Gibbs phase rule. (2) The ultimate components whose chemical potentials are controlled by the surroundings of a local mineral assemblage in a given process, and thus can be set arbitrarily at an arbitrary temperature and pressure. These environmentally controlled ultimate components are essentially open to the given system. They can be present in certain excess phases (pure or impure), or in an unspecified (or hypothetical) state with variable or fixed chemical potentials [2, 47]. This group of components may be regarded as a modification of perfectly mobile components so as to avoid the theoretical difficulties relevant to the mobility of components.

Zen [7] defined two classes of components: initial value components and boundary value components, whose chemical potentials (or activities at fixed T and P) are determined by the initial proportions and the potentials at the boundary of the system, respectively. In this classification, an excess component present in an excess phase is only a limiting case of boundary value components [7].

In the discussions of open systems, Thompson [8] divided all components into two groups: (1) the components whose chemical potentials are externally controlled, i.e. fixed by some medium outside the selected system, (2) all other components. The two groups of components are designated as K-components and J-components, respectively. In this classification, excess components belong to K-components, because the phase equilibrium is subjected to the chemical potentials of the excess components that are consistent with the presence of their corresponding excess phases. In certain petrological systems, K- and J-components correspond in a sense to Korzhinskii's mobile and inert components, respectively. In other petrological systems, a component may be either a K-component or a J-component depending on what are included in the system. Different from others, Thompson [8] gave detailed theoretical explanations and discussions for his classification.

It should be noted that the classifications of Thompson [6, 8] and Zen [7] have difficulty in the identification of components. For example, the O₂ fugacity or SiO₂ activity of a melt, or the concentration (or activity, chemical potential) of CO₂ or H₂O in a metamorphic fluid mixture may be changed by the physicochemical processes in the system under consideration, or by the mass exchange between the system and its surroundings, or by both processes. In these cases, it is very difficult to determine whether the component is a K-component or J-component [9]. Similar problems also exist in the identification of initial value and boundary value components, because they are closely related to the feature whether the system is open or closed during the evolution of the system.

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