

# Paul Niggli and petrology : order out of chaos

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Objektyp: **Article**

Zeitschrift: **Schweizerische mineralogische und petrographische Mitteilungen  
= Bulletin suisse de minéralogie et pétrographie**

Band (Jahr): **68 (1988)**

Heft 2

PDF erstellt am: **21.07.2024**

Persistenter Link: <https://doi.org/10.5169/seals-52064>

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## Paul Niggli and petrology: order out of chaos

by *James B. Thompson, Jr.*<sup>1</sup>

### Abstract

Paul Niggli's early studies of metamorphic rocks in the Gotthard region were followed by experimental investigations at the Geophysical Laboratory. Much of the rest of his career, however, was as an interpreter, transmitter and theoretician of petrology. His successful application of physico-chemical principles to the problems of metamorphic petrology were an essential part of its emergence as a modern science. His lucid expositions, aided by his geometric and algebraic skills have aided many in understanding our science.

In Part II of this paper the author presents a novel treatment of the relationship between invariant and univariant phase equilibria, and linear dependence in the chemographic array of the coexisting phases in composition space. This was a subject of much interest to Paul Niggli. The author hopes that it will honour his memory.

### Part I

As seen by a physicist, or even by a chemist, mineralogy, and especially petrology, the study of the whole rock, are distinctly untidy subjects, perhaps not worthy of the attention of the best of scientific minds! They are also often regarded as purely descriptive sciences for which most of the necessary information has already been gathered.

Paul Niggli, however, could not accept these judgements. In 1947, late in his career, he was awarded the Roebling Medal of The Mineralogical Society of America. Among the philosophical comments in his acceptance speech he recalls that in his youth advisors, aware of his analytical mind, tried to convince him that his abilities could and should be devoted, more profitably, to one or another of the more "fundamental" sciences. He then went on to show how a complex natural phenomenon, such as a thunderstorm, involved an intimate interweaving of electricity, mechanics, and physical chemistry, and that, were one to focus on only

one of these aspects, much would be lost, at least to one who wished, as he did, to understand the event in its entirety.

A rock and the array of minerals in it were clearly a challenge to Paul Niggli. An industrial chemist would probably regard rocks as the results of poor quality control, under improperly monitored conditions, and then as unsaleable products! No laboratory notebooks exist to tell us how rocks were made or by what series of processes. To Niggli, however, as to us, this is their special charm: to read, if possible, in the chemical and crystallographic complexities of their minerals, at least a part of the record of how they came to be.

To him all scientific tools were valid, and all available information was relevant, including especially the geologic setting of their occurrence. The intellectual approach could be that of a mathematician, a physicist, a chemist, a field geologist, an archaeologist, a historian, or that of a detective solving a murder mystery. Such distinctions meant little in the face of a fascinating problem awaiting solution.

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Paul Niggli, however, was acutely aware, that, in the early years of this century, much needed to be done, if petrology and mineralogy were to take full advantage of what was known, even then, about the chemistry and physics of crystalline materials, and about physical chemistry in general.

Thus began a remarkable career, leading to major contributions in many branches of science. Throughout this career, however, he continued his early interest in petrology as shown by the many publications in his later years that were devoted to the subject.

#### METAMORPHIC AND IGNEOUS PETROLOGY

In 1912, after completing a field and laboratory study of metamorphic rocks adjacent to the Gotthard Massif, young Niggli spent two years as one of the first Europeans to do research at the then new Geophysical Laboratory of the Carnegie Institution of Washington, already a leading center for the application of chemistry and physics to the solution of geologic problems. The scientists he met there, N. L. Bowen, G. W. Morey, J. F. Schairer, and others, were inspiring to the young Niggli who, in turn, inspired them! The first publication to come from this visit was a paper, with the physical chemist John Johnston, that appeared in two parts in the *Journal of Geology* for 1913 (the year following Niggli's doctorate). A German version (NIGGLI and JOHNSTON, 1914) appeared the following year in *Neues Jahrbuch*. To readers on both sides of the Atlantic these papers were, though not often referred to today, by far the best treatment then available of the physical chemistry of metamorphic processes. One of my own early papers, published more than forty years later, was a direct consequence of my discovery of this 1913 paper. To me this paper, more than any other, put metamorphic petrology, until then an essentially descriptive science, on a firm theoretical footing. It quickly won converts, among them Ulrich Grubenmann, Paul Niggli's former mentor, who, with his former student as collaborator, completely rewrote his earlier *Die kristallinen Schiefer* (GRUBENMANN, 1904, 1907, 1910) as the classic *Die Gesteinsmetamorphose* of GRUBENMANN and NIGGLI (1924).

While at the Geophysical Laboratory Niggli pursued, with George Morey, an earlier interest in the behaviour of silicate melts with volatile components. Niggli's thinking on igneous petrology and magmatic processes was strongly influenced by his months at the Geophysical Laboratory. Many of his writings served to introduce his European colleagues to the research done there and to its significance to igneous petrology. This culminated in his prize-winning monograph: *Die leichtflüchtigen Bestandteile im Magma* (NIGGLI, 1920a) later revised and enlarged as *Das Magma und seine Produkte* (NIGGLI, 1937).

In the foregoing monographs, and in related textbooks such as *Lehrbuch der Mineralogie* (NIGGLI, 1920b, and later editions), and *Gesteine und Minerallagerstätten* (NIGGLI, 1948, 1952, in part with E. NIGGLI), Niggli's role was essentially to explain and interpret, in other words: to teach. Although he had carried out both field and laboratory investigations early in his career, it is his contribution to our understanding of the researches of others that has been most lasting. Niggli not only produced many eminent students in the usual way, but also had students (like myself) whom he never knew, but who benefitted from his lucid writings. The late D. S. Korzhinskii once remarked to me that his interest in physico-chemical petrology was aroused by reading *Die Gesteinsmetamorphose* as a young man, and that none of the writings of his petrologic forebears had influenced his own development as much as those of Paul Niggli. I am sure that many others have had the same experience, but had not taken the trouble to say so.

#### NIGGLI VALUES

With the aid of students and colleagues Paul Niggli also compiled a vast amount of analytical data on the chemistry of magmatic rocks. A problem faced by all petrologists in undertaking such a task is how to deal with the chemical complexity of a typical rock. One must, in most cases, consider eight to ten major elements, and a host of others in trace amounts. Many schemes for simplifying and condensing this chemical information have been devised. The generalized components of Tab. 1 were first presented by Paul Niggli in 1919 as a modifica-

Tab.1 Composition in Oxide Components to Composition in Niggli Values  
(Reference: NIGGLI, 1919, 1920a)

Niggli Values		Oxide Components (mol units)
si	=	SiO <sub>2</sub>
al	=	Al <sub>2</sub> O <sub>3</sub> + Cr <sub>2</sub> O <sub>3</sub>
fm	=	FeO + MgO + MnO
c	=	CaO
alk	=	Na <sub>2</sub> O + K <sub>2</sub> O
h	=	H <sub>2</sub> O
mg	=	Mg/(Fe + Mg + Mn)
k	=	K/(Na + K)

tion of the earlier system of ALFRED OSANN (1899). These quantities eventually became known as "Niggli Values". They and their geometric representations as a simplified composition space have been widely used, especially by European petrologists. Although the Niggli values and similar schemes appear to have been devised by a mixture of science and intuitive inspiration, it can be shown that they may also be obtained as a formal mapping of multidimensional composition spaces into simpler ones. Thus if we retain the oxide components Na<sub>2</sub>O, CaO, MgO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and H<sub>2</sub>O but replace the oxide components such as K<sub>2</sub>O, FeO, MnO, and Cr<sub>2</sub>O<sub>3</sub>, by the operators (or exchange components): KNa<sub>-1</sub>, FeMg<sub>-1</sub>, MnFe<sub>-1</sub> and CrAl<sub>-1</sub>, then the formulas for transforming an analysis from the "old" set (all oxides) into the "new" set (partly oxides and partly exchange components) are as given in Tab. 2. The values for the "new" oxide components: Na<sub>2</sub>O, CaO, MgO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and H<sub>2</sub>O (now commonly known by the acronym NCMASH) are precisely the principal Niggli values. Exchange operators represent displacement in composition space. By omitting these operators and considering the new NCMASH values we are in effect projecting along them and condensing, or mapping, the multicomponent space into the simpler NCMASH. Because nearly all major rock minerals have end-member compositions at distinctive points in NCMASH, the Niggli values provide for a direct correlation between the chemical analysis and the mode of a rock.

W.L. Bragg (who received the Roebling Medal the year following Paul Niggli) suggested in his book on the *Atomic Structure of Minerals* (BRAGG, 1937) that mineral chemistry could be simplified by considering but one idealized end member per mineral, combined with the various substitutions (exchange components) by which its composition may be varied. This suggestion has been pursued elsewhere (THOMPSON et al., 1982; THOMPSON, 1981, 1982a, 1982b). By condensing mineral compositions onto a single NCMASH or "Niggli Space" end-member it has been possible to construct a vector space in which displacements on heterogeneous reactions and variations in modal abundances may be graphically portrayed.

Tab.2 Composition in Oxide Components to Composition in Mixed Oxide and Exchange Components (References: THOMPSON, 1981, 1982a)

Oxide and Exchange Components:		Original Oxide Components:
SiO <sub>2</sub>	=	SiO <sub>2</sub>
Al <sub>2</sub> O <sub>3</sub>	=	Al <sub>2</sub> O <sub>3</sub> + Cr <sub>2</sub> O <sub>3</sub>
MgO	=	MgO + FeO + MnO
CaO	=	CaO
Na <sub>2</sub> O	=	Na <sub>2</sub> O + K <sub>2</sub> O
H <sub>2</sub> O	=	H <sub>2</sub> O
CrAl <sub>-1</sub>	=	2Cr <sub>2</sub> O <sub>3</sub> - 2Al <sub>2</sub> O <sub>3</sub>
FeMg <sub>-1</sub>	=	FeO + MnO
MnFe <sub>-1</sub>	=	MnO
KNa <sub>-1</sub>	=	2K <sub>2</sub> O

#### SCHREINEMAKERS NETS

Paul Niggli was skilled in both analytical and geometric methods in the application of physical chemistry to petrologic problems. It is clear that he was intrigued by the work of F. A. H. SCHREINEMAKERS (1915-1925) especially the parts relating to the pressure-temperature representation of univariant and invariant equilibria to the arrays of points in composition space representing the compositions of the coexisting phases. In his 1930 exposition of the Schreinemakers approach to invariant

points Niggli could not resist (in his Figs. 3 and 4) pointing out the close analogy between the arrays of points representing rational formulas in composition space and the arrays of points for forms with rational indices in the gnomonic projection of a crystal. The paper then goes on to demonstrate the relation between "chemographic" arrays of points in composition space and the bundles of univariant lines that meet at invariant points (NIGGLI, 1930).

Niggli's fascination with the interplay between geometric and algebraic representations of natural phenomena is as evident in his petrology as it is in his crystallographic work. This has been, to me one of the most attractive aspects of Paul Niggli's scientific legacy. I am sure that Paul Niggli, as a teacher, would hope that his heirs could add to the impressive structure left behind. I shall therefore present, in the second part of this paper, an exposition of the consequences of the linear dependence, in composition space, of an assemblage of phases. It provides a generalized and simplified approach to many aspects of Schreinemakers nets. As such it may be of interest to many who have enjoyed this aspect of Niggli's work.

## Part II

### LINEAR DEPENDENCE

Let us suppose that the phases,  $a, b, c, \dots, \Phi$  are a set having composition such that an equation of the form:

$$0 = AU_a + BU_b + CU_c + \dots = \sum_{\phi} \Phi U_{\phi} \quad (1)$$

can be written where the quantities  $U_a, U_b, \dots, U_{\phi}$  represent the unit quantities of the phases and the quantities  $A, B, C, \dots, \Phi$  are numerical coefficients. These coefficients contain an arbitrary common multiplier and any one may be set at unity if convenient to do so. Equation (1) then represents a *linear dependence* among the composition of the phases. If an equation such as (1) can be written for a given assemblage we shall refer to the assemblage as a *linearly dependent* assemblage. Because the unit quantities,  $U_{\phi}$ , in an equation such as (1) are inherently positive, it is necessary that at least *one* of the coefficients  $A, B, \dots, \Phi$  in (1) has a sign different from the others. If we rearrange (1) by moving all negative terms to the left-hand-side then

the rearranged equation has the form of a statement that the set of phases on the left may be transformed into the set on the right or *vice versa* without altering the compositions of any of the phases involved. Such a transformation thus represents a special type of heterogeneous reaction that may be called a 'phase-reaction' (following the usage of F.A.H. Schreinemakers). In the reactions more usually considered in physical chemistry, stoichiometric equations are written in terms of independently variable (I.V.) *components* of the phases. These independently variable components do not, in general, correspond to the actual compositions of any of the phases. It is however always possible (if convenient) to select *one* of the ones for a given phase so that it does correspond to the actual composition of that phase. It is also possible, if the assemblage is linearly dependent, to select the corresponding phase reaction as *one* of the more general set of independent heterogeneous reactions. Pure substances, however, are special cases. These have but one component, necessarily the composition of the phase. A heterogeneous reaction, involving only pure substances, is thus automatically a phase-reaction.

A special type of phase reaction occurs when all but one of the coefficients in equation (1) have the same sign. The reaction is then said to be terminal to the exceptional or 'interior' phase. In an equilibrium P-T representation, the reactions terminal to a given phase constitute the boundary to its field of stability. In composition space an interior phase is one that is completely enclosed by the polygon, polyhedron or more generalized polytope formed in composition space by the other phases involved in the linear dependence.

Equation (1) may also be regarded as a statement of *material* balance. As written, the left-hand-side is zero. Other properties of the assemblage, however, do not, as a rule, balance in the same way. Thus, if  $\bar{V}_{\phi}$  represents the volume of a unit quantity of phase  $\phi$  we have

$$\Delta V_R = A \bar{V}_a + B \bar{V}_b + C \bar{V}_c + \dots = \sum_{\phi} \Phi \bar{V}_{\phi} \quad (2)$$

stating that for the reaction (1), as written, there may be a net change in volume of  $\Delta V_R$ . Similarly for other thermodynamic properties such as the internal energy,  $E$ , the entropy,  $S$ , the enthalpy,  $H (= E + PV)$ , the Helmholtz energy,  $F (= E - TS)$  and the Gibbs energy,  $G (= E + PV - TS)$  we have

$$\Delta E_R = \sum_{\varphi} \Phi \bar{E}_{\varphi} \quad (3)$$

$$\Delta S_R = \sum_{\varphi} \Phi \bar{S}_{\varphi} \quad (4)$$

$$\Delta H_R = \sum_{\varphi} \Phi \bar{H}_{\varphi} \quad (5)$$

$$\Delta F_R = \sum_{\varphi} \Phi \bar{F}_{\varphi} \quad (6)$$

$$\Delta G_R = \sum_{\varphi} \Phi \bar{G}_{\varphi} \quad (7)$$

The left hand sides of (2) through (6) may vanish under certain conditions, but ordinarily do not. For equilibrium assemblages, however, any stoichiometric relation among the I.V. components of an assemblage must be accompanied by a parallel relationship among the corresponding chemical potentials. Because the compositions of the phases may be selected as components, the  $\bar{G}_{\varphi}$  may be identified with corresponding chemical potentials. With (1) and (7) we have then, for *equilibrium* assemblages:

$$\Delta G_R = \sum_{\varphi} \Phi \bar{G}_{\varphi} = 0 \quad (8)$$

and:

$$\Delta H_R = T \Delta S_R \quad (9)$$

#### COMPONENTS

The composition of the unit quantity of any phase,  $\varphi$ , may be specified in terms of a minimal set ( $c_{\varphi}$  in number) of independently variable (I.V.) components: Thus

$$U_{\varphi} = \sum_i X_{i\varphi} U_i \quad (10)$$

where  $U_i$  is the unit quantity of I.V. component,  $i$ , and  $X_{i\varphi}$  is the unit fraction of that component. In dealing with crystalline phases and their constrained chemical variations, however, it is often impractical, if not impossible, to describe all the phases in terms of the same set of I.V. components. It is also rarely convenient to describe the system as a whole in terms of components that are necessarily I.V. in any of the phases present. We shall therefore introduce a minimal set of components, that are I.V. in a reacting assemblage but that are not necessary I.V. in any of the individual phases. To be I.V. in the assemblage, however, it must be possible to express the unit quantity  $U_s$  of a component,  $s$ , in terms of a set (not necessarily unique) of components,  $i$ , that *are* I.V. in one or another of the individual phases. We have then, for each  $s$ :

$$U_s = \sum_i v_{is} U_i \quad (11)$$

where the  $v_{is}$  are numerical coefficients. Each component,  $i$ , on the other hand, must be specified uniquely in terms of the components  $s$ :

$$U_i = \sum_s v_{si} U_s \quad (12)$$

For a given phase we then have, from (10) and (12)

$$U_{\varphi} = \sum_s \sum_i X_{i\varphi} v_{si} U_s \quad (11)$$

or:

$$U_{\varphi} = \sum_s q_{s\varphi} U_s \quad (14)$$

where:

$$q_{s\varphi} \equiv \sum_i X_{i\varphi} v_{si} \quad (15)$$

Note that the form of (14) mimics that of (10). The components in (10), however, are I.V. in the individual phases whereas those in (14) are necessarily I.V. only in the assemblage as a whole. Note also that the  $q_{s\varphi}$  are linear functions of the  $X_{i\varphi}$ . In certain instances the components  $i$  and  $s$  may be chemically identical, but in general they are not.

#### ASSEMBLAGES CONTAINING A SINGLE LINEAR DEPENDENCE

We may now take note of the fact that a material balance as in equation (1) must also hold for each of the components of the system, taken individually:

$$0 = Aq_{sa}U_s + Bq_{sb}U_s + Cq_{sc}U_s + \dots = (\sum_{\varphi} \Phi q_{s\varphi})U_s \quad (16)$$

or, inasmuch as the  $U_s$  are non-zero, we have, for each component,  $s$ :

$$0 = Aq_{sa} + Bq_{sb} + Cq_{sc} \dots = \sum_{\varphi} \Phi q_{s\varphi} \quad (17)$$

Equation (1) and the equations (17),  $C_s$  in number, may be regarded as homogeneous equations in the variables  $A, B, C, \dots, \Phi$ . If the number of phases,  $N_{\varphi}$ , in the linear dependence is equal to or less than  $(C_s + 1)$  then the number of equations is equal to or greater than the number ( $N_{\varphi}$ ) of variables  $A, B, C, \dots, \Phi$  on their right-hand-sides. For the equations (1) and (17) to be consistent, we must, for the special case  $N_{\varphi} = (C_s + 1)$ , have:

$$\begin{vmatrix} U_a & U_b & U_c & U_d & \cdot & \cdot \\ q_{1a} & q_{1b} & q_{1c} & q_{1d} & \cdot & \cdot \\ q_{2a} & q_{2b} & q_{2c} & q_{2d} & \cdot & \cdot \\ q_{3a} & q_{3b} & q_{3c} & q_{3d} & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{vmatrix} = 0 \quad (18)$$

Expanding (18) by columns we obtain an equation having the form of (1) in which the cofactors of the  $U_\phi$  provide expressions for a consistent set of the coefficients  $A, B, C, \dots, \Phi$  in terms of the  $q_{s\phi}$ . If  $N_\phi$  is less than  $(C_s + 1)$  then there are more equations (17) than are needed for the above result, which may now be obtained by using (1) and any subset,  $(N_\phi - 1)$  in number, that may be selected from equations (17). In the latter case, where  $N_\phi$  is less than  $(C_s + 1)$ , there must be further conditions for consistency having the form:

$$\begin{vmatrix} q_{1a} & q_{1b} & q_{1c} & \cdot & \cdot \\ q_{2a} & q_{2b} & q_{2c} & \cdot & \cdot \\ q_{3a} & q_{3b} & q_{3c} & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{vmatrix} = 0 \quad (19)$$

where the determinant contains *only*  $q_{s\phi}$ . An independent set of equations (19) may be obtained by using the first  $N_\phi$  equations in combination, successively, with each of the remaining ones. This procedure yields  $(C_s - N_\phi + 1)$  independent equations (19). Each of these is a relationship among the  $q_{s\phi}$ , and hence among the  $X_{i\phi}$  that must hold if the linear dependence exists.

We shall refer to the  $(C_s - N_\phi + 1)$  equations (19) as the conditions for linear dependence. Note that, if  $N_\phi$  equal to or greater than  $(C_s + 1)$ , no equations (19) are possible. This is because linear dependence is unavoidable if  $N_\phi = (C_s + 1)$ . If  $N_\phi > (C_s + 1)$  there are then *several* linear dependencies, one for each subset of  $(C_s + 1)$  phases. If  $N_\phi = (C_s + 1)$  we may rewrite equations (14) as

$$0 = U_\phi(-1) + q_{1\phi} U_1 + q_{2\phi} U_2 + \dots \quad (20)$$

There is one equation (20) for each of the  $(C_s + 1)$  phases. Each equation is homogeneous in the variables  $(-1), U_1, U_2, \dots, U_s$ . For their consistency the determinant of the coefficients must vanish:

$$\begin{vmatrix} U_a & q_{1a} & q_{2a} & q_{3a} & \cdot & \cdot \\ U_b & q_{1b} & q_{2b} & q_{3b} & \cdot & \cdot \\ U_c & q_{1c} & q_{2c} & q_{3c} & \cdot & \cdot \\ U_d & q_{1d} & q_{2d} & q_{3d} & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{vmatrix} = 0 \quad (21)$$

Expansion of (21) by rows yields the same result as the expansion of (18) by columns. In the latter case, however, we have not made use of an equation (1) but instead have *obtained* an equation (1) directly from equations (21). If  $N_\phi > (C_s + 1)$  it necessarily follows that there are as many independent equations (21), and hence equations (1) as thus are subsets of the full assemblage that contain  $(N_\phi + 1)$  phases. If  $N_\phi = (C_s + 2)$  there are then  $N_\phi$  equations (1), in each of which *one* of the  $N_\phi$  phases has been omitted.

#### LINEAR DEPENDENCE IN AN EQUILIBRIUM ASSEMBLAGE

For the equilibrium state of a single phase, any intensive property may be regarded as a function of  $(C_\phi + 1)$  others, as a function, for example, of pressure, temperature and  $(C_\phi - 1)$  composition variables. Pressure, temperature, and the chemical potentials of a set of  $C_\phi$  I.V. components are related by a Gibbs-Duhem equation, of which there is one for each phase:

$$\bar{V}_\phi dP - \bar{S}_\phi dT = \sum_i X_{i\phi} d\mu_i \quad (22)$$

In an assemblage of phases in equilibrium at a given pressure and temperature the  $\sum_\phi C_\phi$  chemical potentials are related by conditions of chemical equilibrium. There is one of these for each heterogeneous reaction. The number of independent heterogeneous reactions, in turn, is equal to the number of independent stoichiometric relations that may be written relating the I.V. components of the various phases. These are  $(\sum_\phi C_\phi - C_s)$  in number (see THOMPSON, 1982b for a systematic procedure by which such a set may be obtained). The  $(\sum_\phi C_\phi - N_\phi + 2)$  variables in the Gibbs-Duhem equations are thus related by  $(\sum_\phi C_\phi - C_s)$  equations. The number of independent intensive variables (variance) of the assemblage is then given by:

$$\text{Var} = C_s - N_\phi + 2 \quad (23)$$

This is the classical Gibbs Phase Rule. It does not, however, take into account the possibility of critical phases (not to be considered here), nor does it take linear dependence into account except where the latter is automatic ( $N_\phi > C_s$ ). With a single linear dependence involving  $C_s$  or fewer phases, however, there are ( $C_s - N_\phi + 1$ ) further independent relations (21) among the intensive variables. For any assemblage containing a single linear dependence, and no critical phases, the variance is then given by:

$$\text{Var} = (C_s - N_\phi + 2) - (C_s - N_\phi + 1) = 1 \quad (24)$$

Such an equilibrium assemblage can thus exist only along a unique, univariant line in P-T space. All intensive parameters relevant to such an assemblage therefore have fixed values at any given point on its univariant line. Any reaction that takes place at a given pressure and temperature, in such an assemblage, is therefore one that is associated with a variation in the *amounts* of the phases, but leaves their intensive parameters (including their composition variables) unaltered. It is thus a phase-reaction in the sense of Schreinemakers.

#### THE P-T LINE OF A LINEAR DEPENDENCE

Because of the freedom of choice in selecting components  $i$  and  $s$ , and the correspondence between the chemical equilibrium conditions and the stoichiometric equations, we may obtain the following results, for an equilibrium assemblage, from (14) and (15) respectively:

$$\mu_s = \sum_i v_{is} \mu_i \quad (25)$$

$$\mu_i = \sum_s v_{si} \mu_s \quad (26)$$

also:

$$\bar{G}_\phi = \sum_s q_{s\phi} \mu_s \quad (27)$$

From (26) we have:

$$d\mu_i = \sum_s v_{si} d\mu_s \quad (28)$$

whence:

$$\begin{aligned} \sum_i X_{i\phi} d\mu_i &= \sum_s (\sum_i X_{i\phi} v_{si}) d\mu_s \\ &= \sum_s q_{s\phi} d\mu_s \end{aligned} \quad (29)$$

With (29) we may now replace each Gibbs-Duhem equation by an equation of the form:

$$\bar{V}_\phi dP - \bar{S}_\phi dT = \sum_s q_{s\phi} d\mu_s \quad (30)$$

Multiplying the equation (30), for phase  $a$  by  $A$ , that for phase  $b$  by  $B$ , and so forth, we obtain:

$$\begin{aligned} A\bar{V}_a dP - A\bar{S}_a dT &= \sum_s Aq_{sa} d\mu_s \\ B\bar{V}_b dP - B\bar{S}_b dT &= \sum_s Bq_{sb} d\mu_s \end{aligned} \quad (31)$$

$$\cdot \quad \cdot \quad \cdot$$

$$\Phi\bar{V}_\phi dP - \Phi\bar{S}_\phi dT = \sum_s \Phi q_{s\phi} d\mu_s$$

adding equations (31) together we obtain:

$$\begin{aligned} (A\bar{V}_a + B\bar{V}_b + \dots) dP - (A\bar{S}_a + B\bar{S}_b + \dots) dT \\ = \sum_s (Aq_{sa} + Bq_{sb} + \dots) d\mu_s \end{aligned} \quad (32)$$

With (2), (4) and (17), however, (32) reduces to

$$\Delta V_R dP - \Delta S_R dT = 0 \quad (33)$$

and, with (9), we obtain:

$$\frac{dP}{dT_{ld}} = \frac{\Delta S_R}{\Delta V_R} = \frac{\Delta H_R}{T \Delta V_R} \quad (34)$$

a remarkably concise result that applies to *any* linear dependence. Specific results given in the literature may differ in appearance, but all may be reduced to the simple form of (33)!

#### PASSIVE PHASES

Linear dependence may involve all of the phases in an actual assemblage or only a subset of them. Phases in the larger assemblage that are not part of the linear dependence do not take part in the phase reaction associated with it, and thus may be regarded as *passive* phases with respect to that reaction. SCHREINEMAKERS (1916, p. 515) called these "indifferent" phases but the word has since acquired other meanings, in related contexts, and is therefore best avoided. Because a linear dependence is univariant nearly any further specialization produces invariance. If for example two of the phases in a linear dependency become critically indistinguishable at some point on the univariant line, the line must then terminate there at a critical "end-point".

#### DEGENERACY

The number of passive phases that coexist with a linearly dependent set is also severely



constrained. It is convenient here to consider two systems: a greater one containing the linearly dependent assemblage plus the passive phases, and a lesser one containing only the linearly dependent set. The lesser is thus a subsystem of the greater. Let us designate properties of the lesser system by primes. Let us further designate the number of I.V. components in the greater one, that are not included in the lesser one, by  $C_e$ , and the number of passive phases by  $N_p$ . We then have:

$$C_s = C'_s + C_e \quad (35)$$

$$N_\phi = N'_\phi + N_p \quad (36)$$

If  $C_e$  is greater than zero the linear dependence is in what we may call a *degenerate* subsystem following NIGGLI (1948). These are not uncommon where crystalline phases are present owing to the constraints on their chemical variation. If the addition of a passive phase adds no new components to those already I.V. in the lesser system, we then have a greater system for which there is one more Gibbs-Duhem equation, or equation (30), but no new variables. The greater system is then necessarily invariant. On the other hand, if the passive phase brings one or more extra components then the assemblage remains univariant. More generally the greater system is univariant if  $N_p \leq C_e$  and is invariant if  $N_p = (C_e + 1)$ . If  $C_e > 0$  the linear dependency is in a lesser assemblage that is a degenerate subassemblage of the greater one.

We may now distinguish two general types of invariance:

- (1) If  $N_\phi = (C_s + 2)$ .
- (2) If  $N_\phi < (C_s + 2)$ , but  $N_p = (C_e + 1)$

$$\text{INVARIANCE: } N_\phi = (C_s + 2)$$

With invariance of this type the linear dependencies are inevitable and there must be  $N_\phi$  of them, one associated with each subset of  $(C_s + 1)$  phases. The possibilities have been treated exhaustively in the literature. The treatment presented here is essentially that of SCHREINEMAKERS (1915-1925) but with modifications based on the work of MOREY and WILLIAMSON (1918), PAUL NIGGLI (1930, 1937), D.S. KORZHINSKII (1957, 1959) and some further features first presented here.

Because linear dependencies are automatic if  $N_\phi > C_s$  we may simply write the  $N_\phi$  equa-

tions (14) in the form of (20). The coefficient matrix for this set of equations then has the form of (21) but now has one more row than columns. This coefficient matrix is the "bundle matrix" of KORZHINSKII. It also contains a submatrix, containing only the  $q_{s\phi}$ , that has *two* more rows than columns. This last has, in turn, square submatrices that may be obtained by deleting any pair of rows, say rows  $j$  and  $k$ . The determinants of these square submatrices may then be defined as  $Q_{jk}$  where the subscripts  $j$  and  $k$  indicate the rows deleted.

We may obtain square matrices from the bundle matrix by deleting any one row. We shall also number the rows in order, and take the determinants obtained by deleting the odd-numbered rows as positive and those obtained by deleting even-numbered rows as negative. Expanding these determinants by rows then yields:

$$\begin{aligned} \text{[a]: } 0 &= Q_{ab} U_b - Q_{ac} U_c + Q_{ad} U_d + \dots \\ \text{[b]: } 0 &= -Q_{ab} U_a + Q_{bc} U_c - Q_{bd} U_d + \dots \quad (37) \\ &\cdot \quad \cdot \quad \cdot \quad \cdot \\ &\cdot \quad \cdot \quad \cdot \quad \cdot \end{aligned}$$

and so forth. The coefficient matrix for equations (37) may then be written in the antisymmetric form:

$$\begin{array}{cccccc} & U_a & U_b & U_c & U_d & \cdot & \cdot \\ \text{[a]} & 0 & +Q_{ab} & -Q_{ac} & +Q_{ad} & \cdot & \cdot \\ \text{[b]} & -Q_{ab} & 0 & +Q_{bc} & -Q_{bd} & \cdot & \cdot \\ \text{[c]} & +Q_{ac} & -Q_{bc} & 0 & +Q_{cd} & \cdot & \cdot \\ \text{[d]} & -Q_{ad} & +Q_{bd} & -Q_{cd} & 0 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{array} \quad (38)$$

Although implicit in the work of SCHREINEMAKERS (1915-1925) these matrices were first formalized by PAUL NIGGLI (1937), and we shall refer to them as a "Niggli matrices". The generalized nature of (38), however, is a consequence of the procedures introduced by KORZHINSKII. Degeneracies are indicated by pairs of zeros off the lead diagonal. If  $Q_{jk}$ , for example, is zero there is a linear dependence in which phases  $j$  and  $k$  are passive phases. By the arguments presented earlier a linear dependence is

necessarily in a degenerate subsystem if there is more than one passive phase. The topology of the array of univariant lines, and their metastable extensions, that meet at an invariant point in P-T space may be deduced simply by knowing whether the various  $Q_{jk}$  are positive, negative or zero. PAUL NIGGLI (1930) has enumerated the possibilities for systems of three or fewer components, as illustrations of a procedure that is applicable to a system of any number of components.

The chemographic arrays associated with invariant points of this type ( $N_{\phi} = C_s + 2$ ) correspond to the ways in which  $(C_s + 2)$  points can be arranged in a  $(C_s + 1)$ -dimensional space. Each topologically distinct array produces a topologically distinct univariant bundle meeting at the corresponding invariant point in P-T space. Non-degenerate chemographic arrays are those in which no subset of  $C_s$  or fewer phases is linearly dependent (i.e. coincident, collinear, coplanar etc.) The topology of both the chemographic and P-T arrays is determined by the pattern of signs and zeros in the Niggli matrix. If the array is non-degenerate the matrix has no zeros except in the leading diagonal. The non-degenerate, topologically distinct, P-T arrays for system of three or four components are shown in Fig. 1. There are interesting correspondences between the topologic symmetry of the P-T arrays and those of the chemographic arrays (compare the non-degenerate chemographic arrays for a ternary system in Fig. 2 with the corresponding P-T arrays in Fig. 1).

It is also of interest that these arrays for a  $(c_s + 1)$ -component system may be obtained simply by exploring all possible ways of adding one extra line (and its metastable extension) to each of the arrays for a  $c_s$ -component system. The procedure works in reverse, however, only if those lines that are *not* labeled *i* in Fig. 1 are eliminated. If a line labeled *i* is eliminated the result, in each case, is one of the arrays in the bottom row of Fig. 1. This appears, at first sight, to make little sense, but further investigation shows that the reactions labeled *i* are the ones in which the phase that does not participate is an interior phase. The adjacent stable boundaries represent, in each case, reactions that are terminal to that phase. The arrays in the bottom row of Fig. 1 thus represent vertices on the boundary of the field of stability of a phase *i* in P-T space.

$$\text{INVARIANCE: } N_{\phi} < (C_s + 2); N_p = (C_e + 1)$$

Invariance of this type is maybe understood by noting that the coefficients A, B, C, ...  $\Phi$  in equation (1) may vary from point to point along the corresponding univariant curve. If there is a point at which one of these coefficients, say  $\Phi$ , passes through zero, the phase reaction passes from the form

$$(a + b + \dots) + \phi = (m + n + \dots) \quad (39)$$

on one side of the special point, to the form

$$(a + b + \dots) = (m + n + \dots) + \phi \quad (40)$$

on the other. At the special (invariant) point the reaction is of the form

$$(a + b + \dots) = (m + n + \dots) \quad (41)$$

in which  $\phi$  is now a passive phase. The last of these, however, must represent a point on a lesser linear dependence, one that does not involve phase  $\phi$ . From the point of view of the lesser dependence, phase  $\phi$  is a passive phase in the same chemical system. The univariant line for this lesser dependence must therefore pass through the same point. Because the same equation (33) must apply to their slopes, we may conclude that the two curves are tangent at that point. Since there is no corresponding constraint on higher derivatives the two curves should osculate – that is: kiss but not cross – at the invariant point. The lesser linear dependence must therefore be wholly on one side of the greater. Once so placed, however, we find that it must be metastable on one side of the invariant point, and stable on the other as indicated in Fig. 3. This is because the reaction in crossing the right-hand limb of the greater, in the direction of the lesser, is here terminal to the phase *b*. The adjacent limb of the lesser linear dependence is therefore metastable. An invariant point of this type requires at least three phases and at least two components (Fig. 3). Fig. 4a shows two such points in the system Fe-O – one where magnetite and liquid of the same compositions coexist with gas and the other where hematite and liquid coexist with gas. The temperature-composition diagram for this system, at one atmosphere, is shown in Fig. 4b.

For *more* than one of the coefficients in (1) to pass through zero, at a point on the curve of the greater linear dependence, it is necessary that the lesser linear dependence lie in a degen-

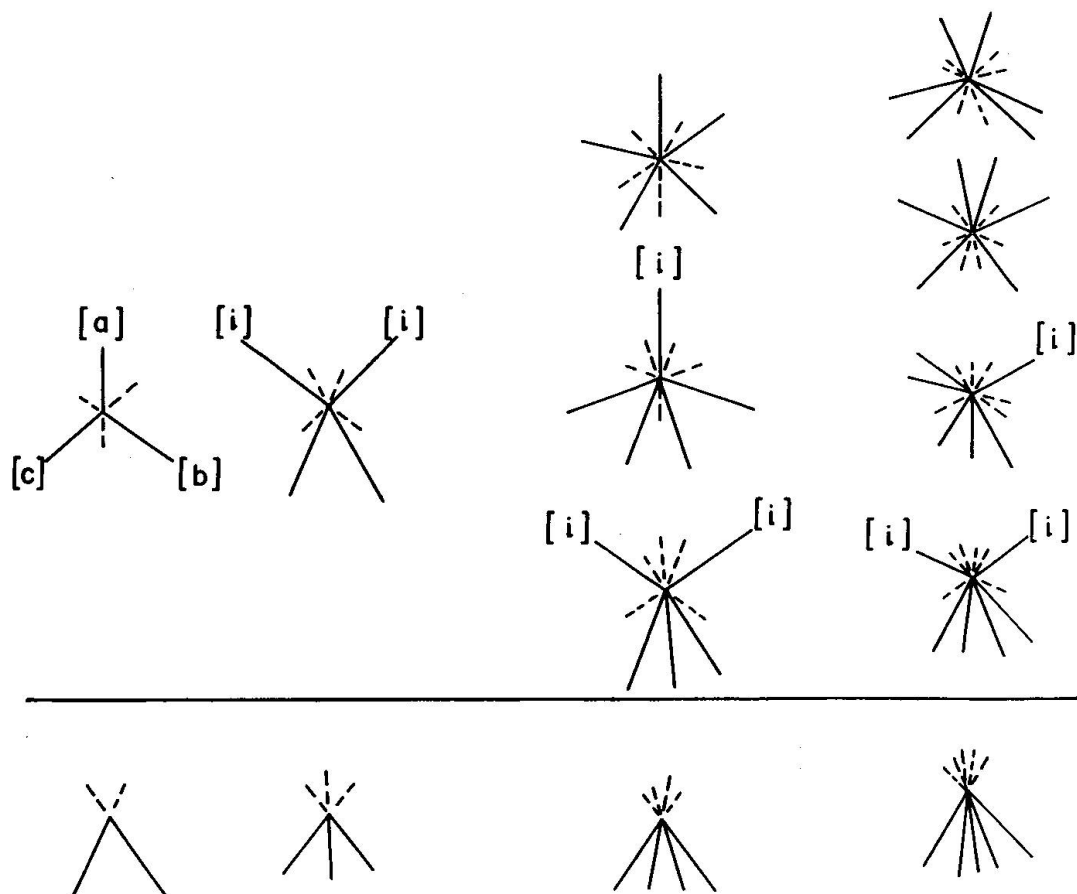


Fig. 1 Non-degenerate, pressure-temperature arrays of univariant lines meeting at invariant points ( $N = C_s + 2$ ) for systems of four or fewer components. Metastable extensions are dashed. Lines labeled [i] are those in which an interior phase, i, does not participate in the reaction (see text). In the one-component triple point, the phases labeled a, b, c are all interior phases. Deletion of a line labeled [i] or [a, b, c] leads in each case to the array shown below the horizontal line. Deletion of other lines from quadruple, quintuple or sextuple points yields one of the arrays in the next column to the left.

erate subsystem of fewer I.V. components. This is because there is more than one passive phase, and hence  $C_e$  must be greater than one. An invariant point of this kind requires at least four phases and at least three components. The lesser dependence must then lie in a two component subsystem. Two possibilities arise: either the coefficients that vanish at the invariant point have the same initial sign or they do not. In the first instance the reactions on the two limbs of the greater linear dependence may be written, for one side, as:

$$(a + b + \dots) + (j + k + \dots) = (m + n + \dots) \quad (42)$$

and, for the other, as:

$$(a + b + \dots) = (m + n + \dots) + (j + k + \dots) \quad (43)$$

The reaction associated with the lesser is:

$$(a + b + \dots) = (m + n + \dots) \quad (44)$$

Either limb of the greater is thus terminal to one of the essential assemblages of the lesser, and hence one limb of the latter must be metastable. In the second instance the reactions by the two limbs of the greater are:

$$(a + b + \dots) + (j + k + \dots) = (m + n + \dots) + (s + t + \dots) \quad (45)$$

and:

$$(a + b + \dots) + (s + t + \dots) = (m + n + \dots) + (j + k + \dots) \quad (46)$$

$$(a + b + \dots) = (m + n + \dots) \quad (47)$$

In this second instance neither limb of the greater linear dependence has a phase-reaction that is terminal to a sub-assemblage that is essential to the lesser. Both limbs of the lesser are therefore stable. Simple examples of both types are shown in Fig. 5 for hypothetical ternary sys-

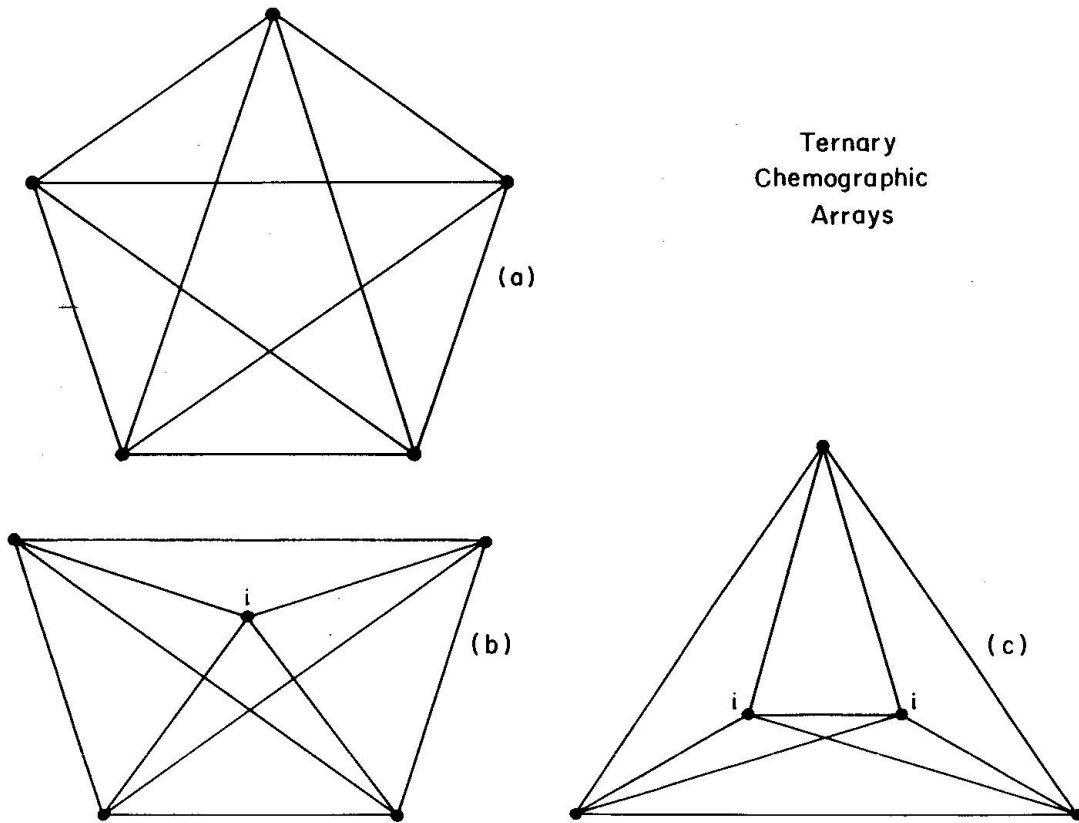


Fig. 2 Chemographic arrays, idealized to show full topologic symmetry, for non-degenerate, ternary quintuple points. Their correspondence with the P-T arrays of Fig. 1 is given by the number of interior phases, *i*.

tems. In both, the lesser linear dependence is in a binary subsystem. The orientation of the line of the subsystem relative to the compositions of the other phases is the key to the difference.

It should be noted that all the invariant points just considered, where  $N_\phi < (C_s + 2)$ , involve a lesser linear dependence contained within a greater one. If the lesser linear dependence contains more than one fewer phases than the greater, then the lesser is necessarily in a degenerate subsystem.

DISCUSSIONS IN THE EARLIER LITERATURE

Univariant lines where  $N_\phi = (C_s + 1)$  and invariant points where  $N_\phi = (C_s + 2)$  have received extensive treatment elsewhere. Most of the more significant references have already been cited, and the references in these provide a guide to the rest.

Univariant lines where  $N_\phi \leq C_s$  have not received as much attention. Notable exceptions include the writings of PALATNIK and LANDAU

Linear Dependencies

- (1)  $0 = AU_a - BU_b + CU_c$
- (2)  $0 = AU_a - BU_b$
- (3)  $0 = AU_a - BU_b - CU_c$

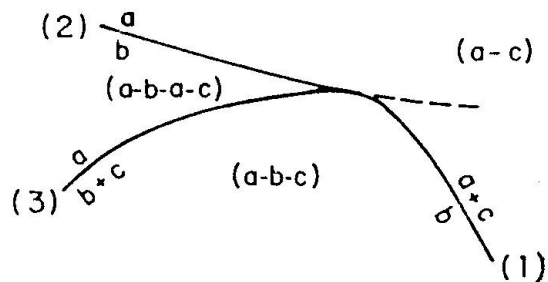


Fig. 3 Pressure-temperature array associated with an invariant, two-component, three-phase equilibrium in which two of the three phases coincide in composition. The right hand limb of (2) is metastable because (1) is terminal to phase *b*. The sequence of phases along the composition coordinate is shown in parentheses for each divariant field about the invariant point.

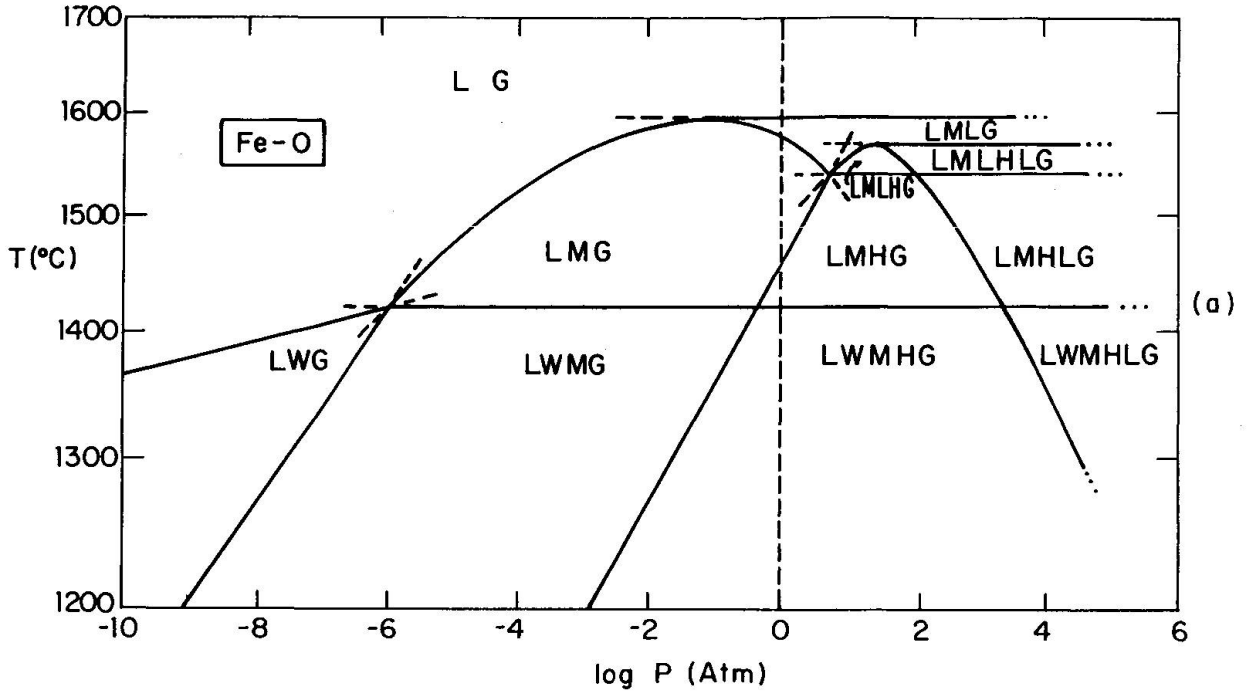


Fig. 4a Pressure-temperature diagram for the system iron-oxygen, based on DARKEN and GURRY (1953) and CROUCH ET AL., (1971). The sequence of phases (from Fe to O) in each divariant field is shown by the initial letters of the phases shown below in (b).

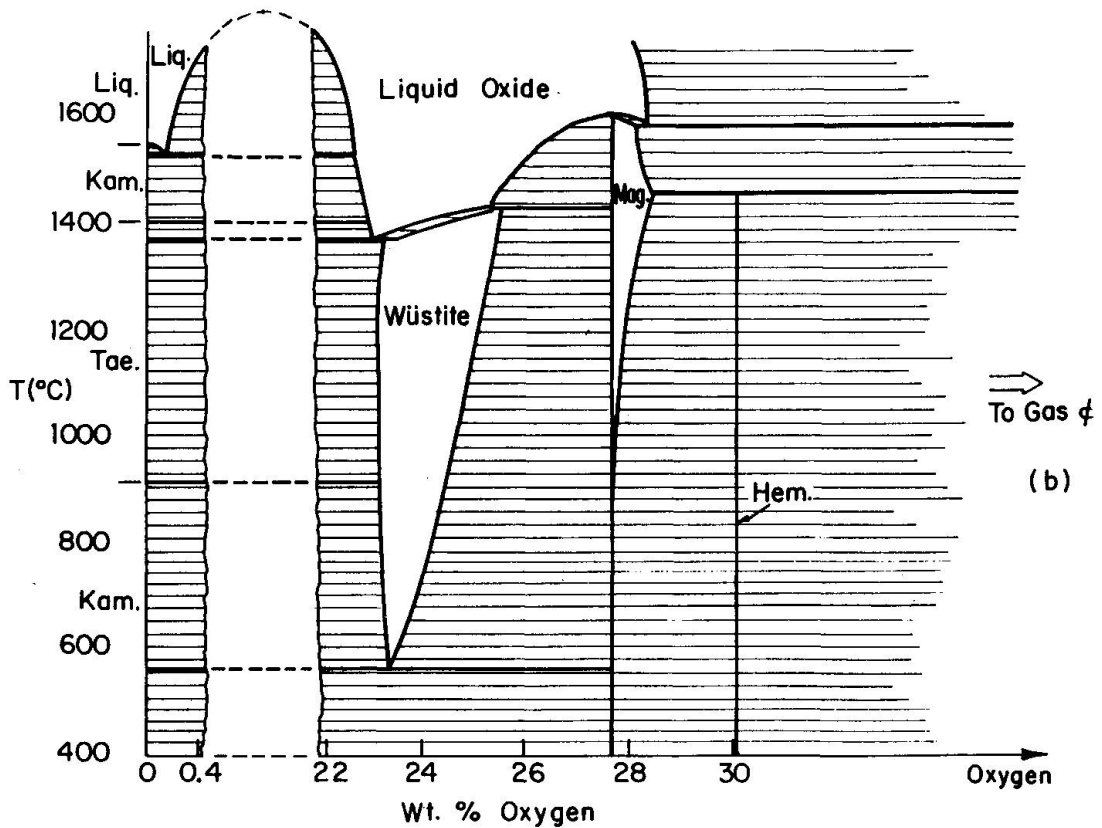


Fig. 4b Temperature-composition diagram, modified from DARKEN and GURRY, for the same system at one atmosphere. This diagram has two non-degenerate quadruple points, and two invariant points of the type illustrated in Fig. 3.

Liq., Kam., Tae., Hem., and Mag. refer to liquid, kamacite, taenite, hematite and magnetite, respectively.

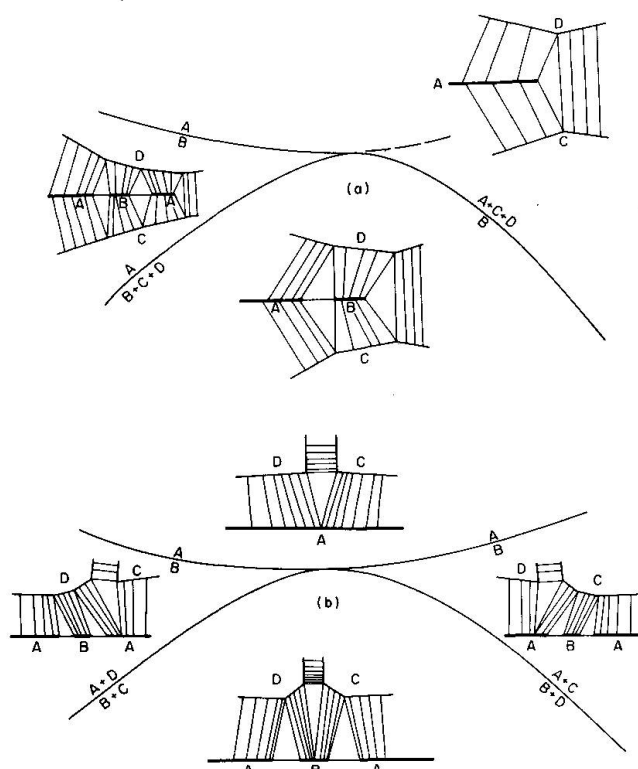


Fig. 5: Pressure-temperature array for invariant points in hypothetical ternary systems in which the "greater" linear dependence (see text) has two passive phases, C and D. The lesser, binary linear dependence involves only the two phases, A and B. They are confined to the degenerate binary subsystem. In (a) phases C and D switch sides of the reaction in the same sense, and in (b) they switch sides in the opposite sense, as the greater linear dependence is followed through the invariant point. The sketches, in the divariant regions, show, in each case, an appropriate chemographic array.

(1961, 1964, especially Chapter V) and SOBELMAN (1964). Another exception is the monograph by PRIGOGINE and DEFAY (1950, 1957) where such matters are treated in Chapters XVIII, XXVIII and XXIX. Readers may find the terminology of Prigogine and Defay confusing, however, in that the word "indifferent" is used in a quite different sense than that of Schreinemakers. An "indifferent state" in the Prigogine and Defay terminology is one in which a phase-reaction may take place, in other words a state that includes a linear dependency. Another source of confusion is that their "variance" is simply the variance of the classical phase rule, *without* the additional constraints of the linear dependency being taken into account. This leads to rather laborious wording and to convoluted explanations.

The Gibbs-Konovalow theorem (see also WILLIAMSON and MOREY, 1918 and KORZHINSKII, 1958) is in fact a rather obvious result of the univariance of linear dependencies for which  $N_{\phi} \leq C_s$ . If  $dP = 0$  then  $dT = 0$  and *vice versa*. If an assemblage varies *across* such a linear dependence, at constant  $P$ , then, for any other intensive property,  $x$ , we have, at the crossing:  $dx/dT = 0$ . At constant  $T$ :  $dx/dP = 0$ . Many statements of the Gibbs-Konovalow theorem, however, are too strong. The results just given imply only a *stationary* value of  $x$  under isobaric or isothermal conditions. This is often also an *extreme* value but is *not necessarily* so. One example, familiar to petrologist, will suffice: In the liquidus diagram for the anhydrous "granite system" (SCHAIRER, 1950), at one atmosphere, the saddle point on the alkali feldspar liquidus is a linear dependence where an alkali feldspar and a liquid have the same composition. The liquid coexisting with feldspar is clearly at a stationary but not an extreme value!

Two papers by H.J. GREENWOOD (1967, 1968) also deal with problems of linear dependence. Greenwood, however, was concerned primarily with the problem: Given an assemblage of phases; how do we determine whether or not it contains a linear dependence? The question addressed here, however, is: Given a linear dependence, what are its consequences?

#### Acknowledgements

Much of the content of this contribution has been sharpened by discussions, over the years, with students and colleagues. I should like, however, to mention especially the contributions of Takashi Fujii in extended discussions, some years ago, of the Niggli matrix, and those of George W. Fisher in more recent discussions on the general matter of linear dependence.

A preliminary version of much of the second part of this paper was presented at the John Hopkins University in Baltimore, Maryland, in May 1988, at a symposium in memory of Hans. P. Eugster. Hans Eugster, an eminent geochemist and petrologist, was one of the last students to work under the direct supervision of Paul Niggli. At the time of his death (in December, 1987) Hans was planning his own contribution for presentation at the Niggli symposium.

I first knew Hans in the early 1950's when he was a post-doctoral visitor at the Massachusetts Institute of Technology and at the Geophysical Laboratory, and I was a newly-appointed member of the faculty

at Harvard. It was at this time that Hans brought to my attention many of the contributions of Paul Niggli that have influenced my own later work so strongly.

I also wish to thank Martin Engi for invaluable assistance with the manuscript and to give my special thanks to Ernst Niggli, gracious host on two extended visits to Berne and source of insight on the life and career of his father.

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