THE SEQUENCE OF P-T CURVES AROUND A QUATERNARY INVARIANT POINT IN THE SYSTEM $NaAlSiO_4-KAlSiO_4-SiO_2-H_2O$

A THEORETICAL DISCUSSION

Ki-Tae Kim *

ABSTRACT

The system $NaAlSiO_4-KAlSiO_4-SiO_2-H_2O$, Bowen's "Petrogeny's Residua System" of course is extremely important in understanding the phase relationships of igneous and metamorphic rock in the continental crust. The phase relationships in this system, however, have not been completely established in the P-T range above the Mohorovicic discontinuity. They need to be established.

In this study, the most probable sequence of P-T curves around a quaternary invariant point($\sim$5Kb/$\sim$635°C) in the system using Schreinemakers' rule, is deduced, essentially on the basis of Morse's(1969a and b) experimental data. Possible modifications of the sequence of the P-T curves considering likely changes of the invariant chemogram are also considered. It is concluded that the sequence of P-T curves around the invariant point ($\sim$5Kb/$\sim$635°C) is (L), (Anl), (Or), (V), (Ne) and (Ab) on the P-T projection, where the P-T curve (L) is extended towards lower P-T regions, and the (Anl) curve is extended towards a region of higher temperature and lower pressure from the invariant point respectively.

I. INTRODUCTION

By inspecting Morse's (1969 a and b) experimental data, an approximate invariant chemogram in the system $NaAlSiO_4$-$KAlSiO_4$-SiO_2-H_2O was derived. In order to establish phase relations on the P-T plane, one of the most important steps is to decide on the configuration of the invariant chemogram, if an invariant point exists in the studied P-T range.

In the present study, the most probable invariant chemogram was constructed using the estimated compositions of six invariant

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* Institute of Geophysics and Planetary Physics, University of California, Los Angeles, California 90024

phases, albite, orthoclase, nepheline, analcite, liquid and water vapor, mainly taken from Morse's experimental data. The sequence of the P-T curves around the invariant point (∼5Kb/∼635°C) wear inferred from the available data and Schreinemakers' rule (1916).

By allowing the composition points of the invariant phases to move within a range of the component space in a manner considered reasonable on the basis of available pata reporʒed by various authors, other conceivable P-T diagram types were generated.

II. THE SEQUENCE OF P-T CURVES AROUND THE INVARIANT POINT

Morse(1969 a) determined a liquidus diagram and several isobaric-isothermal sections at $P_{H_2O}=5Kb$ in the silica-undersaturated region of the system $NaAlSiO_4-KAlSiO_4-SiO_2-H_2O$. He estimated an invariant point to be located at some pressure not far below 5Kb and at a temperature not far above 635°C.

At the supposed invariant point(approximately 5 Kb and 635°C), the compositions of the six invariant phases, albite, orthoclase, nepheline, analcite, liquid and water-vapor, are reasonably estimated by the author to be as shown in Table I, largely on the basis of Morse's data (1969 a, p. 116-118; 1969 b, p. 121). Assuming these phase-compositions to be approximately correct(at least their topological relations to be acceptable), an invariant chemogram was constructed in a regular tetrahedron defined by the four components, $NaAlSiO_4$, $KAlSiO_4$, SiO_2 and H_2O. As shown in Fig. 1, the chemogram is a monoconcave octahedron, according to the definition of Schreinemakers (1916, p. 824). It can be also defined as a "hexa-hedron" with one interior phase point, in a fashion similar to Zen(1966, p. 24) who described a monoconcave pentagon

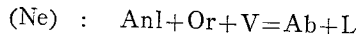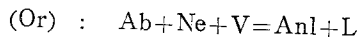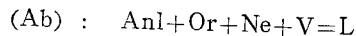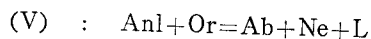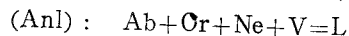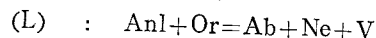(Schreinemaker) as "quadrilateral with one interior phase point".

TABLE 1. THE COMPOSITIONS OF THE INVARIANT PHASES AT A QUATERNARY INVARIANT POINT (5 Kb and 635⁺°C) IN THE SYSTEM $NaAlSiO_4-KAlSiO_4-SiO_2-H_2O$, APPROXIMATELY ESTIMATED FROM THE DATA OF MORSE (1969a, p. 116-118; 1969b, p.121).

Equilibrium phases	Composition Wt. %	
	Anhydrous Composition	H_2O-Content
Ab (Albite s. s.)	$Ne_{50}. Ks_5. Qz_{45}$	—
Or(Orthoclase s. s.)	$Ne_{17}. Ks_{39}. Qz_{44}$	—
Ne(Nepheline s. s.)	$Ne_{83}Ks_{13}Qz_4$	—
Anl(Analcite s. s.)	$Ne_{67}Ks_3Qz_{30}$	8
L(Liquid)	$Ne_{53}Ks_{19}Qz_{28}$	11*
V(Vapor)	Dissolved solid 5%**	95

* The H_2O-solubility in the melt is estimated from data determined by Kim & Burley (B, Fig. 4a) on the theoretical basis given in section V-2, ibid.

** The dissolved solid in the ternary invariant vapor phase in the system $Ab-Ne-H_2O$ reported by Peters, Luth & Tuttle (1966, p. 741) is used.

Since there is no compositional degeneracy in the chemogram, the six univariant reactions must be unique and as presented below:

(L)   : $Anl+Or=Ab+Ne+V$
(Anl) : $Ab+Or+Ne+V=L$
(V)   : $Anl+Or=Ab+Ne+L$
(Ab) : $Anl+Or+Ne+V=L$
(Or) : $Ab+Ne+V=Anl+L$
(Ne) : $Anl+Or+V=Ab+L$

where the phase in parentheses is the missing phase in the univariant reaction, following Schreinemakers' notation.

By using Morse's experimental data, the following relations of the P-T curves were deduced.

i) Two univariant curves (Ab) and (Ne) are situated between 600°C and 640°C at 5Kb.
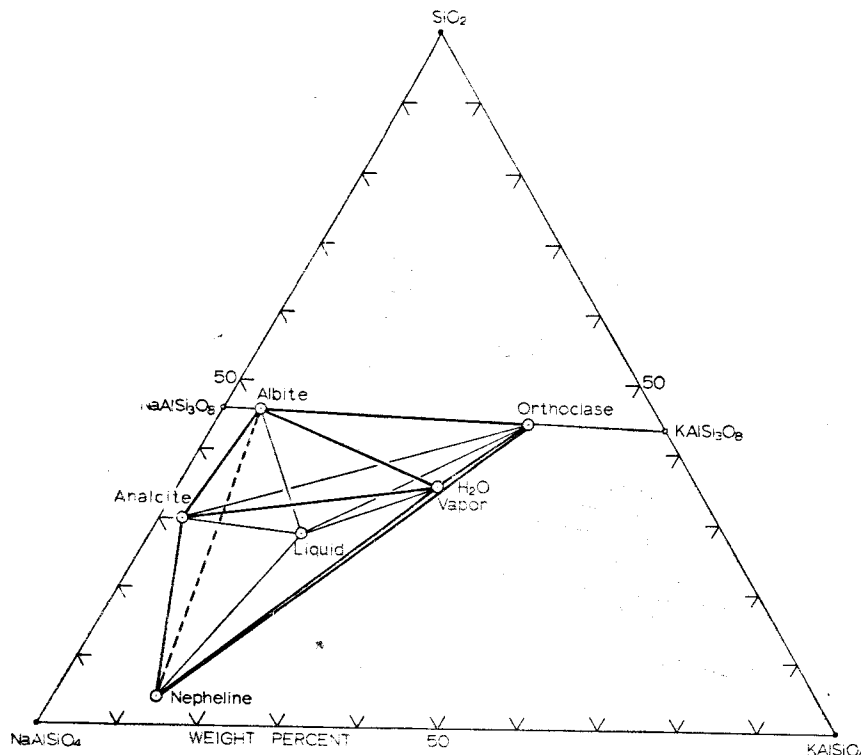
FIG. 1. A QUATERNARY INVARIANT CHEMOGRAM IN THE SYSTEM $NaAlSiO_4$-$KAlSiO_4$-SiO_2-H_2O.

The compositions of the invariant phases are those most probably assumed on the basis of the data reported by Morse (1969 a & b). H_2O is towards the reader. The chemogram is a monoconcave octahedron (or a hexahedron with an interior phase).

ii) A univariant curve (L) extends towards the region of lower temperature and lower pressure from the invariant point.

iii) Two univariant curves (Anl) and (Or) exist at the higher temperature side from the invariant point.

As shown in Fig. 2, the P-T diagram type consists of one one-curvical bundle (only one (L) univariant curve), one two-curvical bundle (two univariant curves (Or) and (Anl)) and one three-curvical bundle (three curves (Ab), (Ne) and (V)), and agrees with the relations deduced above.

III, EIGHTEEN POSSIBLE P-T DIAGRAM TYPES

In the previous section, the sequence of P-T curves around an invariant point was deduced on the basis of a reasonably assumed chemogram. Now the available data are reviewed further.

According to Morse's liquidus diagram (1969 a, p. 116) the minimum temperature of melting in the ternary system without the potash component is located at about the composition $NaAlSi_2O_6$. The peritectic boundary curve is situated in the albite field instead of in the nepheline field. In the ternary system $NaAlSi_3O_8$-$NaAlSiO_4$-H_2O, however, both invariant analcite nd the liquid comdositions are much richer in the nepheline-component (Peters, Luth and Tuttle, 1966, p. 741; Kim & Burley, 1971 A, Table V) than those of Morse. The peritectic point is located by these
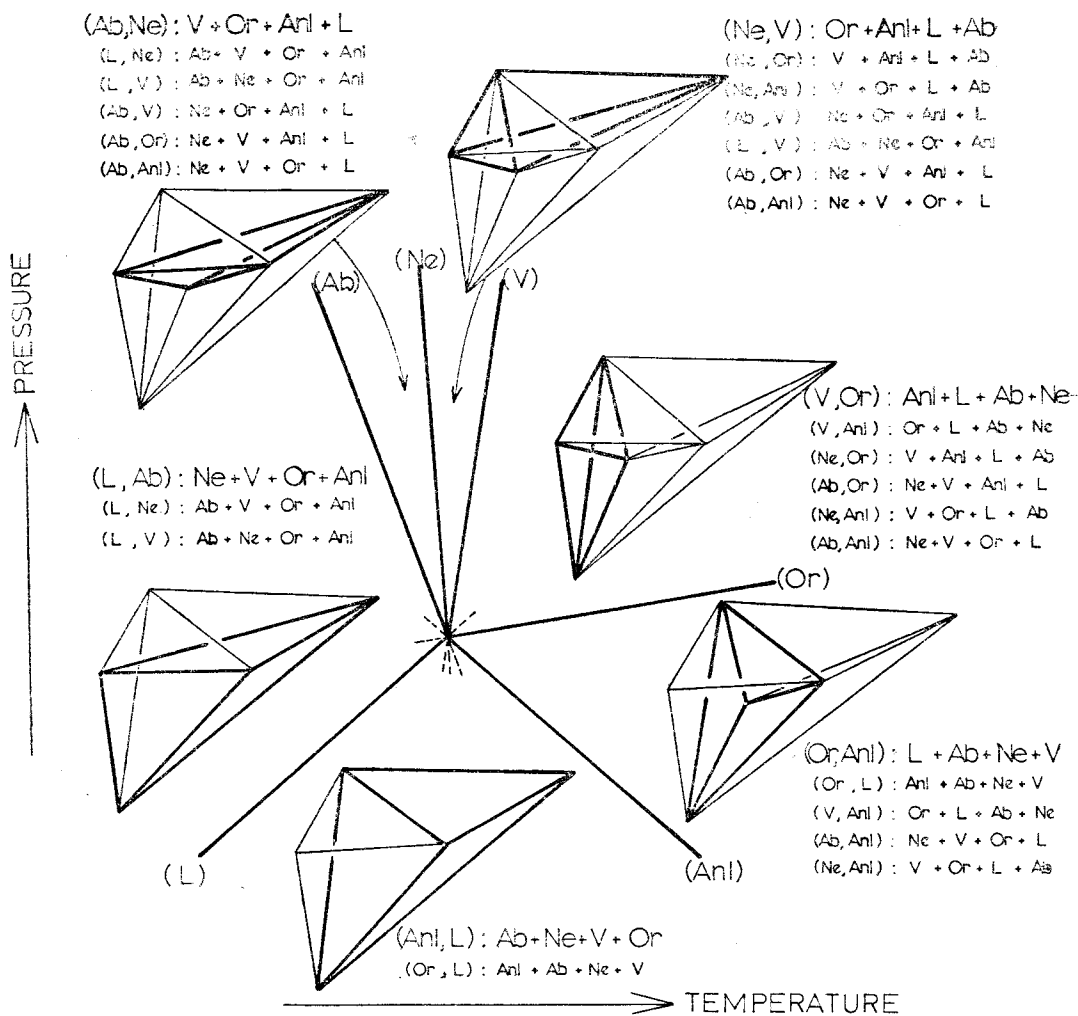
FIG. 2. THE SEQUENCE OF P-T CURVES AROUND THE INVARIANT POINT(5 Kb & 635°C)
IN THE SYSTEM $NaAlSiO_4$-$KAlSiO_4$-SiO_2-H_2O.

The sequence is deduced on the basis of the invariant chemogram shown in Fig. 1. Tie-
trahedra represent divariant phase-assemblages in the immediate vicininity of the supposed
invariant point. The tetrahedron drawn with thick solid lines is a representative divariant
phase-assemblage several divairant ones given in the diagram.

authors in the nepheline-stability field, con-
trary to that of Morse. The compositional
trend of liquidus analcites during progressive
differentiation of the Square Top intrusive
rocks (Wilkinson, 1965, p. 438, Fig. 5) is in
good agreement with the experimental results
in the system $NaAlSi_3O_8$ $NaAlSiO_4H_2O$

Thus, it is possible that the true analcite

composition at the quaternary invariant point
is richer in the nepheline-component than
that estimated on the basis of Morse's results.
The invariant albite and K-feldspar may also
be slightly richer in the two components
$NaAlSiO_4$ and $KAlSiO_4$ instead of being on
the $NaAlSi_3O_8$–$KAlSi_3O_8$ join(Kim & Burley,
1971A, Figure 11) and so on.

In order to approach the real invariant chemogram (at least topologically the correct one), it is necessary to move some or all of the six invariant phases within reasonably restricted compositional regions in the four component space. For the sake of simplicity, we will move only the analcite phase point within a somewhat enlarged area instead of
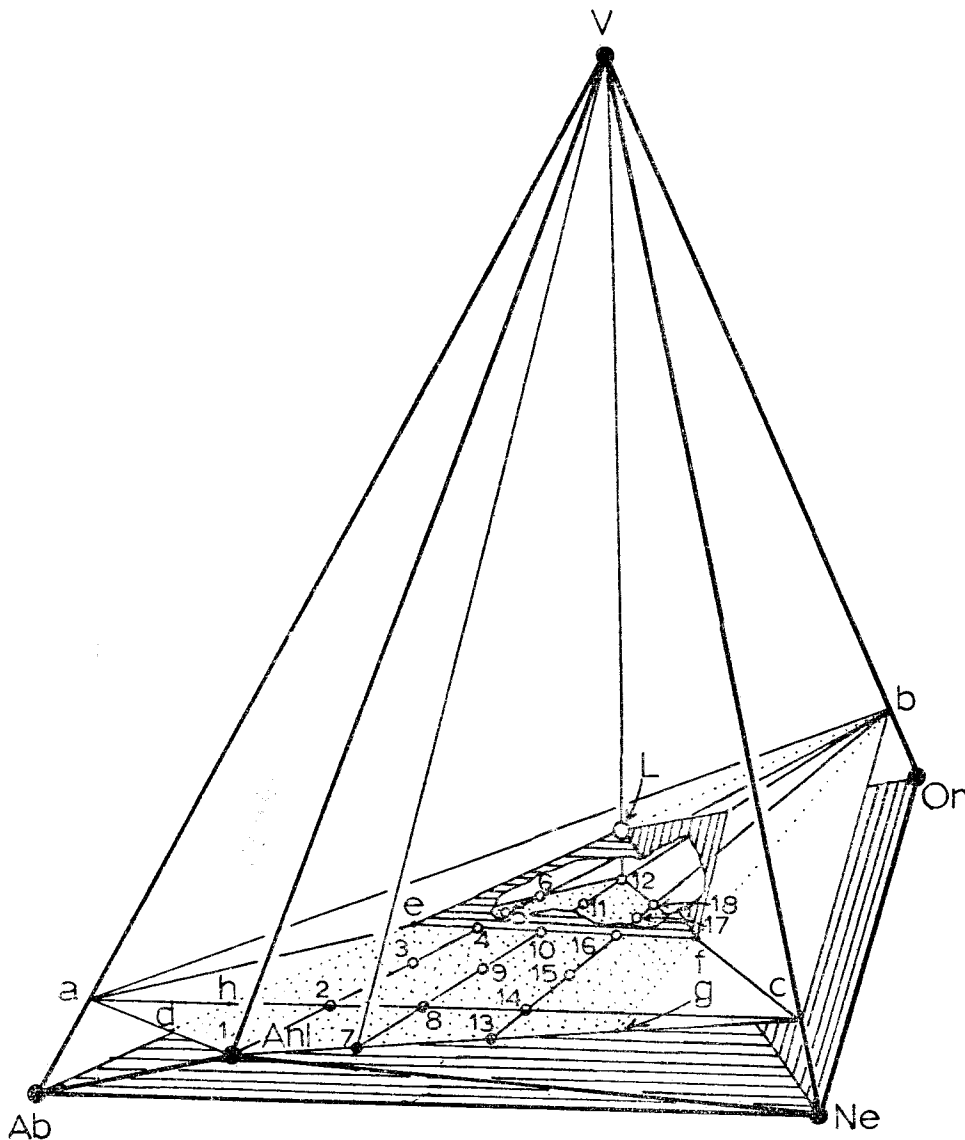
FIG. 3. EIGHTEEN DISTINCT CHEMOGRAPHIC RELATIONS OF INVARIANT PHASES.

When the composition point of analcite is allowed to move in a hexagon (stippled area) defined by six points d, e, 12, f, g, & l, infinite invariant chemograms are produced, but they are topologically classified into eighteen distinct chemogram types. Each of the eighteen analcite points denoted by small circles with numbers is responsible for a distinct type of chemograms. Note that the quadrilateral defined by four points, a, b, c & l is an isohydrous plane (8 Wt % H₂O) on which the hexagon lies, and the hexagon is an open set with respect to two edges d–e & f–g.

moving all the phase points.

For this purpose, the compositional area of the invariant analcite is allowed to vary as described below.

a) The analcite's compositions are all assumed to contain 8 weight percent H_2O. In Fig. 3, therefore, the plane defined by points a, b, c and 1 is an isohydrous plane on which analcite points are allowed to lie.

b) The analcite-phase point is restricted to lie in a hexagon defined by six points d, e, 12, f, g, and 1 (stippled area).

Since the probability of the analcite being located on either of the two edges d-e and f-g of the hexagon is very small, the two edges are excluded from the present consideration. In other words, the hexagon is an open set with respect to these two edges, but closed with respect to the other four edges. This elimination appears meaningless. By this, however, it is possible to reduce the compositional area of the analcite to an extremely narrow area along a line defined by two points 7 and 12 without losing any possible invariant chemogram types.

There are, of course, an infinite number of analcite points in the hexagonal area (stippled area). But only 18 phase points of analcites represent distinct invariant chemogram types. Accordingly, there are 18 possible P-T diagrams. For example, any arbitrary analcite point(e.g. No. 3) which belongs to an open quadrilateral defined by four points, h, 8, 10 and e, produces uniquely one and only one invariant chemogram type. Likewise, any analcite point(e.g. No. 4) on an open line-segment defined by two points, e and 10, also defines one and only one invariant chemogram type. Thus, 18 distinct analcite phase-points are presented as small open circles accompanied with numbers in Fig. 3.

There are two most critical planes with respect to the position of the analcite composition; one of them is the plane defined by the three phase points Or, V and L, and the other one is the one defined by Ab, Ne and V.

With respect to the former reference plane Or-V-L, the eighteen possible chemogram types are grouped into three principal categories. The six analcite points from number 7 to 12 are located on the reference plane. Accordingly, any invariant chemogram which has an analcite with such a composition must be degenerate due to the compositional coplanarity of the four phases, Or, Anl, L and V. These types may be called a "degenerate group". The six analcite points from number 1 to 6 are located in the albite-rich region, and constitute an albite-rich group. The remaining six analcite points from unmber 13 to 18 are located in the nepheline-rich region, and form a nepheline-rich group.

Depending on the composition of analcite relative to the other reference plane Ab-Ne-V, the eighteen chemograms are also grouped into three principal shapes, monoconcave octahedron (points 1, 7 and 13 in Fig. 3), monoconcave hexahedron (points 2, 8 and 14), and biconcave otcahedron(the remaining twelve analcite points).

However, the former reference plane (Or-V-L) is more convenient than the latter plane, for diagrammatic summarization of the eighteen possible P-T diagram types (see Figure 4).

In each of the three P-T diagrams in Fig. 4, the five P-T curves (Anl), (L), (Ab), (Ne) and (V) are fixed and the remaining one (Or) is variable. The relative position of the (Or) univariant P-T curve is defined in the P-T diagram by the position of the analcite phase in the invariant chemogram, i.e. its composition. A few examples suffice to
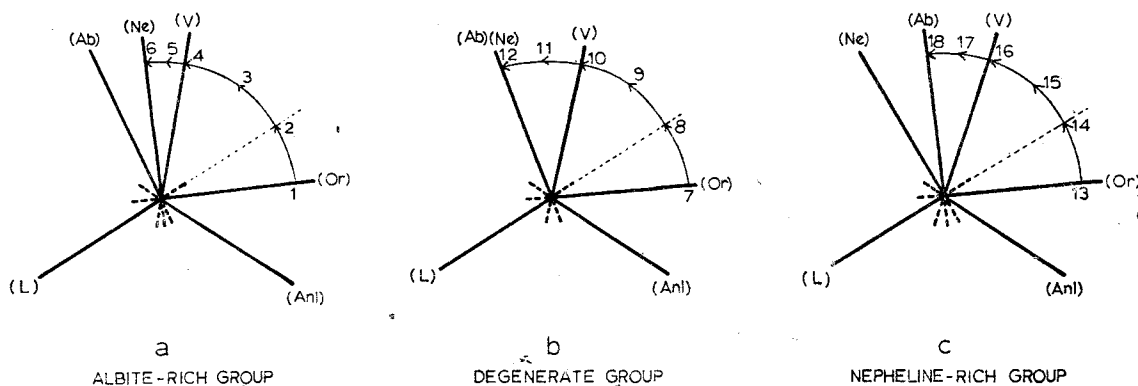
FIG. 4. THREE PRINCIPAL GROUPS OF P-T DIAGRAM TYPES.
The 18 possible P-T diagram types are diagramatically summarized by the 3 principal groups, each of which contains 6 distinct P-T diagram types. In each diagram, the relative positions of (Anl), (L), (Ab), (Ne) & (V) are fixed, and the remaining P-T curve (the (Or) univariant) is movable in its position. The position in the P-T diagram is defined by the relative position of analcite in the chemogram (See Fig. 3).

explain it. In Fig. 4a, the P-T diagram with the (Or) univariant curve at position 1 is formed by an invariant chemogram which has its analcite composition at point 1, in Fig. 3. The P-T diagram with the (Or) curve at position 2 is produced by an invariant chemogram with its analcite composition at point 2, and so on.

Six of the eighteen possible invariant chemograms are non-degenerate systems. Consequently, each of the corresponding P-T diagrams consists of six distinct P-T curves. The chemograms which have the analcite positions as odd numbers (1, 3, 5, 13, 15 and 17) belong to this category.

The remaining twelve invariant chemograms are degenerate systems. Accordingly, at least two univariant cvrves of each P-T diagram are either coincident to each other or one of them corresponds to the metastable prolongation of the other.

1. Albite-rich Group:

Six analcite positions (1, 2, 3, 4, 5 & 6) located in the albite-rich zone from the reference plane Or-V-L (Fig. 3) belong to this group. An invariant chemogram containing each of these analcites derives a distinct P-T diagram type. If the position of the analcite composition is moved from 1 to 6 through the positions 2, 3, 4 and 5, then six P-T diagrams which are distinct from one another with respect to the position of the (Or) univariant curve will be derived successively, shown as arrow marks in Fig. 4 a.

2. Degenerate Group:

The six possible analcite positions(7, 8, 9, 10, 11 and 12) are located on the reference plane Or-L-V in the chemogram(Fig. 3). Therefore, each of the six chemograms has at least a compositional coplanarity of four phases, Anl, Or, L and V. Accordingly, in each of the P-Tdiagrams which belong to this group, it is prerequisite that the (Ab) univariant curve is coincident to the (Ne) one (Fig. 4b). The chemogram having the position of analcite at 12 has the highest degree of compositional degeneracy; one colinearity (Anl, L and V) and three coplanarities(Ab, Anl, L&V; Ne,

Anl, L&V; Or, Anl, L&V). In this case, the three unvariant curves, (Ab), (Ne) and (Or). coincide with one another.

3. Nepheline-rich Group:

The remaining six analcite points (13-18) are located in the nepheline-richer zone relative to the reference plane Or-L-V. The sequences of P-T curves characterized by such chemograms is determined by the analcite position from 13 to 18 (see Figs. 3 and 4c).

In this way, the eighteen possible P-T diagram types are summarized by three principal groups.

IV. CONCLUSION

The six non-degenerate P-T diagram types are the most probable ones among the eighteen possible types, because the remaining twelve degenerate types are very special cases.

According to present knowledge, it is not expected that the invariant analcite contains large amounts of $KAlSiO_4$-component in solid solution. This has been fully discussed in a previous paper (see Kim & Burley, 1971A,). The four invariant chemograms which have analcite positions at 1, 3, 13, and 15 respect-
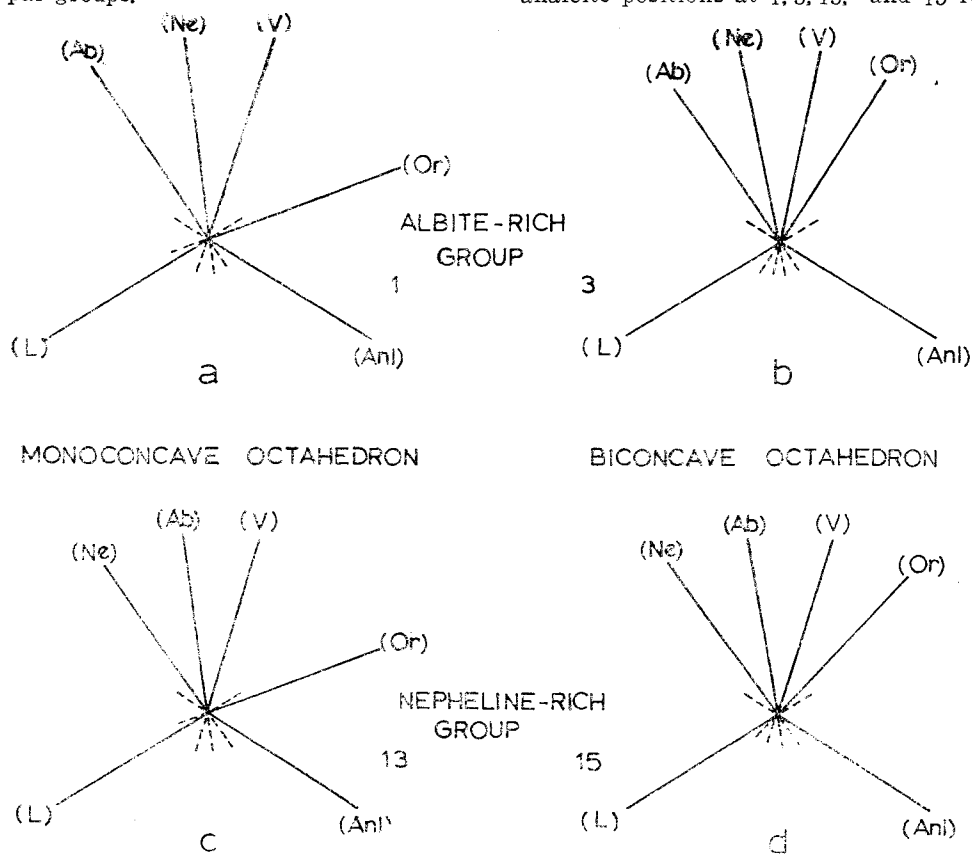

FIG. 5. THE MOST PROBABLE FOUR P-T DIAGRAM TYPES.
The upper two P-T diagram types, a & b, belong to the albite-rich group, and the lower two, c & d, belong to the nepheline-rich group. a, b, c & d were deduced on the basis of the possible invariant chemogram types which have analcite compositions 1, 3, 13 & 15 (in Fig. 3) respectively. The invariant chemogram types of a & c are monoconcave octahedrons (or hexahedrons with an interior phase-point), and the ones of b & d are both biconcave octahedrons (or tetrahedrons with two interior phase-points).

ively, are therfore most probable, and their corresponding P-T diagram types are given in Fig. 5. The P-T diagram type presented in Fig. 5a corresponds to that of Fig. 2, the latter being the one deduced essentially on the basis of Morse's experimental data as previously mentioned. The other three P-T diagram types in fig. 5 b, c & d are essentially the same as the first one (Fig. 5a, & also Fig. 2). For example, the sequence of the P-T curves of the P-T diagram type (Fig. 5b) is exactly the same as that of Fig. 5a, but the only difference between them is in the type of curvical bundles. Between the two P-T diagram types, Fig. 5a & c, the curvical bundle types are the same but the relative position of (Ne) & (Ab) are different, and so on.

Considering only the sequence of P-T curves, the only modification that might be made in the future is the relative position of the (Ab) P-T curve with respect to the (Ne) curve. This will only be solved by experiment.

We have discussed 18 possible P-T diagram types through an exhaustive discussion, but we have returned to the original point (P-T diagram given in Fig. 2). Thus, it is concluded that the sequence of P-T curves around the invariant point($\sim$5Kb/$\sim$635°C) is (L), (Anl), (Or), (V), (Ne) and (Ab) successively on the P-T projection. The P-T curve(L) is exten ded towards the lower P-T region and the (Anl) curve is extended twoards the region of higher temperature and lower pressure respectively from the invariant point. However, the relative position between(Ab) and (Ne) will be reversed if the invariant analcite belongs to the nepheline-rich group of analcites.

ACKNOWLEDGEMENTS

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LIST OF FIGURES

FIG. 1. A QUATERNARY INVARIANT CHEMOGRAM IN THE SYSTEM NaAlSiO$_4$-KAlSiO$_4$-SiO$_2$-H$_2$O.

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FIG. 5. THE MOST PROBABLE FOUR P-T DIAGRAM TYPES.

The upper two P-T diagram types, a & b, belong to the albite-rich group, and the lower two, c & d, belong to the nepheline-rich group. a, b, c & d were deduced on the basis of the possible invariant chemogram types which have analcite compositions 1, 3, 13, & 15(in Fig. 3) respectively. The invariant chemogram types of a & c are monoconcave octahedrons (or hexahedrons with an interior phase-point), and the ones of b & d are both biconcave octahedrons (or tetrahedrons with two interior phase-points).

NaAlSiO$_4$-KAlSiO$_4$-SiO$_2$-H$_2$O 4成分系의
不變點附近의 P–T 曲線의 變移

金 起 泰

Bowen의 "Petrogeny's Residua System"으로 알려져 있는 NaAlSiO$_4$-KAlSiO$_4$-SiO$_2$-H$_2$O系는 大陸地殼에 있어 火成岩과 變成岩 間의 相의 關係를 理解하는데 대단히 重要한 것이다. 그럼에도 불구하고 이 系內의 相의 關係는 아직 Mohorovicic 不連續面 以上의 位置의 P—T 範圍의 것 조차 完全히 알려져 있지 않다.

그러므로 이 相들 間의 關係를 알 必要가 있다. 本 研究는 Schreinemaker 法則을 적용한 系 內에 있는 不變 點 (∼5kb/∼635°C) 附近에 있는 순서를 推理하였는데 이는 主로 Morse (1969a&6) 실험자료에 근거하였다. 結 論으로 不變點 (∼5kb∼635°) 附近에서의 P—T 曲線의 順序는 各各 P—T 投影에서는 (L), (Anl), (Or), (V), (Ne), 및 (Ab)의 順이고 P—T 曲線 (L)은 P—T 區域 下部로 연장되며 (Anl) 曲線은 不變點 보다 높은 溫 度와 낮은 壓力의 區域으로 延長된다는 것을 알았다.