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Mineral reactions in closed systems involving amphibole and plagioclase

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ABSTRACT

Reactions are derived involving solid solutions of amphibole and plagioclase as well as end-members of spinel, olivine, orthopyroxene, clinopyroxene, and quartz. Reactions in progressively more complex systems are developed, starting with four and ending with six components. In this succession, amphibole and plagioclase are first taken as pure end-members or as solid solution of intermediate but fixed composition and then as binary solid solutions of variable composition. The incorporation of pargasite into tremolite is described by the exchange parameter x

$$Na_xCa_2Mg_{5-x}Al_{3x}Si_{8-2x}O_{22}(OH)_2.$$

Plagioclase is a binary solid solution of albite ($y = 1$) and anorthite ($y = 0$)

$$Na_yCa_{1-y}Al_{2-y}Si_{2+y}O_8.$$

The stoichiometric coefficients of reactants and products are expressed in terms of x and y and the positions in reaction space derived where they become zero. This is the position where a phase changes from being produced to being consumed. Depending on the dimensions of reaction space, the zeroth is a point on a reaction line where one compositional variable is displayed, it is a straight or curved line in a reaction square or a plane or surface in a reaction cube where three exchange parameters are shown. If mineral compositions from natural systems are plotted into the reaction space, a reaction path is obtained.

The method has been applied to a mafic replacement pegmatite from the Bushveld Complex.

INTRODUCTION AND PREVIOUS WORK

Indications for a reaction relationship among mineral phases are changes in mineral proportions as well as compositions. Both changes may be continuous and dependent upon each other. The theory of continuous reactions has been presented by Thompson (1982a, 1982b) and Thompson et al. (1982).

Previous to the work cited, reactions were normally written for minerals of fixed composition. The number of phases required to establish a univariant reaction is given by the phase rule (Denbigh, 1971) and depends on the number of components;

$$p = c + 2 - f.$$

If the system contains more phases than required to establish a univariant reaction, different reaction configurations may be possible. These are arranged according to Schreinemakers rules (Zen, 1976) in diagrams where the axes are intensive variables that control the Gibbs free energy of the phases involved. This approach has been applied to multisystems of up to four components and seven phases (Stout, 1990) and is not restricted to end-members only but may include solid solutions of intermediate but fixed composition (Korzhinskii, 1959, p. 107 ff.). In real systems, qualitative reactions may be inferred from textural relationships. Stoichiometric coefficients are determined using mineral analyses as provided by electron microprobe. The use of real mineral compositions restricts the reaction to a specific rock and formation condition, whereas end-member reactions allow a more general application.

The present approach combines features of Schreinemakers method (Zen, 1976) with features of the continuous reaction theory (Thompson, 1982b). Similar to the latter approach, the variation in mineral compositions is described with the aid of exchange vectors. The binary system of tremolite-pargasite (Tr, Prg) for example may be described by the exchange parameter x using the mineral formula

$$Na_xCa_2Mg_{5-x}Al_{3x}Si_{8-2x}O_{22}(OH)_2$$

which is obtained by adding equal quantities of $NaAl\square_{-1}Si_{-1}$ [edenite (ed)] and $AlAlMg_{-1}Si_{-1}$ [tschermakite (tk)] to tremolite. In order to distinguish between Thompson's and the present approach, x in the mineral formula will

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be called exchange parameter, instead of exchange vector. Exchange parameters are variables ranging from 0 to 1. The principal differences between the two methods are in (1) how a reaction equation is written, (2) how stoichiometric coefficients are expressed, and (3) how reaction space is established.

Thompson's reaction equations are written in vector notation. Stoichiometric coefficients are real numbers obtained from solving the matrix of mass balances. Reaction space is established with the stoichiometric coefficients of additive components as well as exchange vectors. In the present approach, mineral compositions in reaction equations and therefore stoichiometric coefficients are expressed by exchange parameters. As a consequence, stoichiometric coefficients are not real numbers, but variables. Depending on the values of the exchange parameter, the mineral stoichiometry may either be positive or negative, thus being consumed or produced. Of main interest will be the position where the coefficient becomes zero. The different possible arrangements of minerals in a reaction equation, the minerals being either produced or consumed, give rise to different reaction configurations, comparable to the combination of phases in the Schreinemakers method (Zen, 1976). However, the different possibilities of arranging mineral phases in a reaction equation do not result from excess phases in a multisystem but from changing mineral compositions (exchange parameters) in a univariant system. The types and number of mineral phases remain constant.

The reaction space defined herein is based on the coordinate system of exchange parameters. This is different from Thompson's approach. Where exchange parameters become zero or one, minerals become pure end-members. This is the case at the corners of reaction space, places where Schreinemakers rules apply. This is similar to Thompson's method. The correct mineral reaction is derived using textural evidence. Both methods can be applied to closed and open systems and, in the latter case, may provide constraints on the mass transfer of ionic species. In this study, only cases for a closed system are presented. The results of this study also have applications in experimental petrology where the bulk composition is fixed. In experimental studies, the knowledge of mineral compositions may provide information on the reaction path and, in favorable cases, enables the estimation of thermodynamic data. It is not restricted to solid solutions of amphibole and plagioclase but may be applied to other rock systems. The main limitation of this approach is graphical and therefore limited by the three dimensions of reaction space.

In the following discussion, the method is developed starting with a four component, five phase system and ending with six components and seven phases. By progressing from simple to more complex systems, the development of stoichiometric coefficients relative to mineral compositions is illustrated. Mineral abbreviations follow the suggestions by Kretz (1983). Amphibole will be abbreviated by Am.

MINERAL REACTIONS AND STOICHIOMETRIC COEFFICIENTS

Four components, zero solid solutions

The system considered first consists of four components, CaO, MgO, SiO_2, H_2O, and the phases tremolite, diopside, enstatite, forsterite, quartz, and an aqueous fluid. According to the phase rule, five phases are required to establish a univariant reaction. Six are present so that one must be excluded for the formulation of a reaction. The maximum number of equations equals the number of phases (Zen, 1966). Degeneracies may reduce this number. In this case, the excluded phase may only be forsterite, enstatite, or quartz because diopside and H_2O are required to balance Ca and hydroxyl in tremolite. The exclusion of diopside would necessitate the replacement of tremolite by anthophyllite; the exclusion of H_2O (the fluid phase) would cause the disappearance of amphibole. Therefore tremolite, diopside, and the fluid are indispensable for the equation, whereas forsterite, enstatite, and quartz can be substituted for a multisystem. The distinction between the two phases is of importance with respect to the stoichiometric coefficients, as will be shown below. The number of reactions equals the number of phases that can be substituted for

$$\text{(Ol)}\qquad \mathrm{Tr} = a\mathrm{Di} + b\mathrm{En} + c\mathrm{Qtz} + \mathrm{H_2O} \tag{1}$$

$$\text{(Opx)}\qquad \mathrm{Tr} = a\mathrm{Di} + b\mathrm{Fo} + c\mathrm{Qtz} + \mathrm{H_2O} \tag{2}$$

$$\text{(Qtz)}\qquad \mathrm{Tr} = a\mathrm{Di} + b\mathrm{Fo} + c\mathrm{En} + \mathrm{H_2O}. \tag{3}$$

The stoichiometric coefficients are listed in Table 1 in the column labeled 4/0 (four components/zero solid solutions).

Five components, one solid solution

The fractional substitution of tremolite by pargasite requires the two additional components Na_2O and Al_2O_3. At least one more phase is required to establish a univariant reaction and to supply the two components in a closed system. The additional phase can be plagioclase with the exchange vector $NaSiCa_{-1}Al_{-1}$. The exchange in amphibole is $NaAl_3\square_{-1}Mg_{-1}Si_{-2}$. The compositions of plagioclase and amphibole are expressed as $Na_yCa_{1-y}Al_{2-y}Si_{2+y}O_8$ and $Na_xCa_2Mg_{5-x}Al_{3x}Si_{8-2x}O_{22}(OH)_2$, with exchange parameters varying between 0 and 1. The system now contains six components and seven phases (plagioclase, amphibole, diopside, enstatite, forsterite, quartz, and the fluid phase). Two phases, for which the stoichiometries are determined first, contain Na and Al; three phases contain Ca, allowing the determination of the stoichiometry of diopside; four phases contain Mg; and six phases contain Si. As before, indispensable and substitutable phases are distinguished. Amphibole, plagioclase, and H_2O belong to the former group; forsterite, enstatite, and quartz belong to the latter. If diopside is assigned to the substitutable phases, Na, Ca, and Al have to be balanced exclusively between amphibole and plagioclase in the reaction (Cpx) and therefore not only de-

TABLE 1. Stoichiometric coefficients

Components/solid solutions		4/0	5/1	6/2	6/3
Reaction	Mineral	Stoichiometric coefficients			
(Ol)	Pl		$2x$	x/y	x/y
	Cpx	2	$2 - x$	$2 - x/y + x$	$2 - x/y + x$
	Spl			$2x - x/y$	$(2x - x/y)/z$
	Opx	3	3	$3 - 4x + 2x/y$	$3 + 2x - x/y - 6x/z + 3x/yz$
	Qtz	1	$1 - 5x$	$1 - x - 2x/y$	$1 - 7x + x/y + 6x/z - 3x/yz$
(Opx)	Pl		$2x$	x/y	x/y
	Cpx	2	$2 - x$	$2 - x/y + x$	$2 - x/y + x$
	Spl			$2x - x/y$	$(2x - x/y)/z$
	Ol	1.5	1.5	$1.5 - 2x + x/y$	$1.5 + x - x/2y - 3x/z + 1.5x/yz$
	Qtz	2.5	$2.5 - 5x$	$2.5 - 3x - x/y$	$2.5 - 6x + x/2y + 3x/z - 1.5x/yz$
(Qtz)	Pl		$2x$	x/y	x/y
	Cpx	2	$2 - x$	$2 - x/y + x$	$2 - x/y + x$
	Spl			$2x - x/y$	$(2x - x/y)/z$
	Ol	−1	$5x - 1$	$x - 1 + 2x/y$	$7x - 1 - x/y - 6x/z + 3x/yz$
	Qtz	5	$5 - 10x$	$5 - 6x - 2x/y$	$5 - 12x + x/y + 6x/z - 3x/yz$

termine the stoichiometry of plagioclase ($a = 4$) but also the composition of feldspar ($y = 0.5$) and amphibole ($x = 2$). Since the exchange parameter of amphibole is outside the allowed composition range, diopside is assigned to the indispensable phases. Balancing Na and Al between amphibole and plagioclase provides not only the stoichiometry of feldspar (Table 1) but also its composition ($y = 0.5$). The fixed plagioclase composition is a reflection of a fixed Na/Al ratio in amphibole (⅓) and therefore this ratio is also fixed in the (closed) system. Consequently, the two components Na_2O and Al_2O_3 degenerate to one component, $NaAl_3O_5$. Originally, there were six components and seven phases, allowing one univariant reaction. The decay of two components to one transforms the system to a multisystem where, again, three reactions, excluding degenerate cases, are encountered:

$$\text{(Ol)}\quad Am(x) = aPl(y = 0.5) + bDi + cEn + dQtz + H_2O \tag{4}$$

$$\text{(Opx)}\quad Am(x) = aPl(y = 0.5) + bDi + cFo + dQtz + H_2O \tag{5}$$

$$\text{(Qtz)}\quad Am(x) = aPl(y = 0.5) + bDi + cFo + dEn + H_2O. \tag{6}$$

The stoichiometric coefficients are given in Table 1 (column 5/1). Although the composition of plagioclase is fixed ($y = 0.5$), that of amphibole (x) may vary from 0 to 1. The stoichiometric coefficients in Table 1, therefore, only balance the above-mentioned equations if y is set equal to 0.5. The coefficients of the four-component system discussed previously can be obtained by setting $x = 0$ (i.e., Am = Tr) in the five-component system.

Six components, two solid solutions

The constant plagioclase composition ($X^{Pl}_{An} = 0.5$) of the previous example can be avoided in two different ways. Either a new phase is introduced containing Na_2O or Al_2O_3, or both, or an already existing phase is allowed to form a solid solution with an end-member containing Na or Al, or both. If one more mineral is added to the system, the increase in the number of phases parallels an increase in the number of components. $NaAl_3O_5$ is split into the two components Na_2O and Al_2O_3, and the multisystem is preserved. The incorporation of a Na- or Al-containing component into an already existing phase would leave the number of minerals unchanged but would increase the number of independent components by one. Only a single reaction would be possible. In order to carry on the multisystem of the previous example, spinel ($MgAl_2O_4$) is introduced as an additional phase. The system now contains six components and eight phases and includes the following reactions:

$$\text{(Ol)}\quad Am(x) = aPl(y) + bDi + cEn + dSpl + eQtz + H_2O \tag{7}$$

$$\text{(Opx)}\quad Am(x) = aPl(y) + bDi + cFo + dSpl + eQtz + H_2O \tag{8}$$

$$\text{(Qtz)}\quad Am(x) = aPl(y) + bDi + cEn + dSpl + eFo + H_2O. \tag{9}$$

Stoichiometries are given under column 6/2 in Table 1. The coefficients now also depend on the composition of plagioclase (y). If y is set equal to 0.5, the stoichiometric coefficients decay to those of the five-component system and the stoichiometric coefficient of spinel becomes zero.

Six components, three solid solutions

Often spinel contains more Fe than Mg, and it seems appropriate in some cases to use hercynite (Hc) instead of spinel. The previous Mg subsystem is replaced by the Fe subsystem. Also, spinel (sensulato) is normally characterized by considerable variation in Al. In the following discussion, hercynite will be substituted by magnetite. In order to avoid the addition of one more component, which would be O_2 in the presence of magnetite, the solid solution of spinel is set to be

$$Fe(Al_zFe_{1-z})_2O_{3+z}.$$

The transformation of divalent to trivalent Fe is not taken into account. This is acceptable only as long as the chemical balancing of elements is considered. The reaction is therefore not suitable for thermodynamic modeling. Magnetite is treated as Fe_3O_3. The stoichiometric coefficients of the reactions

$$\begin{aligned}
&(\mathrm{Ol}) \quad \mathrm{Am}(x) = a\mathrm{Pl}(y) + b\mathrm{Hd} + c\mathrm{Fs} \\
&\qquad + d\mathrm{Spl}(z) + e\mathrm{Qtz} + \mathrm{H_2O} \qquad (10) \\
&(\mathrm{Opx}) \quad \mathrm{Am}(x) = a\mathrm{Pl}(y) + b\mathrm{Hd} + c\mathrm{Fa} \\
&\qquad + d\mathrm{Spl}(z) + e\mathrm{Qtz} + \mathrm{H_2O} \qquad (11) \\
&(\mathrm{Qtz}) \quad \mathrm{Am}(x) = a\mathrm{Pl}(y) + b\mathrm{Hd} + c\mathrm{Fs} \\
&\qquad + d\mathrm{Spl}(z) + e\mathrm{Fa} + \mathrm{H_2O} \qquad (12)
\end{aligned}$$

are given under column 6/3 in Table 1. Again degeneracies are disregarded.

The addition of the binary spinel solid solution changes the stoichiometries of spinel, fayalite, ferrosilite, and quartz. However, the stoichiometries of plagioclase and hedenbergite are not affected because the coefficients of these two minerals were determined using the mass balances for Na and Ca. These elements are not part of spinel or any phase other than amphibole, plagioclase, and clinopyroxene. Similar to amphibole, hedenbergite, and feldspar, spinel is an indispensable phase. The stoichiometries of the 6/3 multisystem decay to those of the 6/2 multisystem by setting $z = 1$.

The distinction between indispensable and substitutable phases has its implications for the stoichiometries. The first type has fixed stoichiometry in a certain multisystem, whereas the stoichiometry of the second depends on the configuration of other substitutable phases present in the reaction equation (see Table 1).

Amphibole has so far been treated as a binary solid solution of tremolite and pargasite. The composition space (Thompson, 1982a) can be extended to more complex solutions. Using end-member molecules listed by Deer et al. (1974, p. 155, Table 16), the following mineral formula is obtained:

$$\mathrm{Na}_{2u+y+2z+w}\mathrm{Ca}_{2-z-2u-2v}\mathrm{Mg}_{5-2u+2v-2x+w}\mathrm{Al}_{4x+y+2u-w}\text{-}\mathrm{Si}_{8-2x-y}\mathrm{O}_{22}(\mathrm{OH})_2.$$

The variables u [glaucophane (gln)], v [cummingtonite (cum)], w [eckermanite (eck)], x (tk), y (ed), and z [richterite (ric)] are 0, (½), and 1 in the limiting cases of pure end-members.

REACTION SPACE AND ZEROTHS

The stoichiometric coefficients in Table 1 are dependent on x, y, and z and were generated by the addition of components and phases to the (4/0) multisystem. A system with a large number of components may degenerate to one with fewer components by setting exchange parameters equal to zero or equal to one to obtain pure end-member reactions. If stoichiometric coefficients equal zero, the conditions are defined where a mineral changes its status from positive to negative in a reaction equation. The same is true for stoichiometries becoming infinite, as will be shown below. These locations in reaction space are defined as zero positions or zeroths in the following discussion.

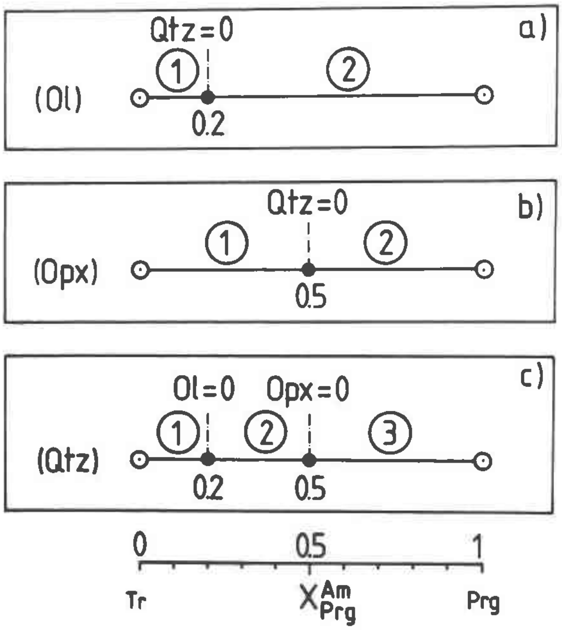

Fig. 1. Zeroths on the reaction line defined by $X^{\mathrm{Am}}_{\mathrm{Prg}}$. The points are located at $X^{\mathrm{Am}}_{\mathrm{Prg}} = 0.2$ for Qtz = 0 in (Ol), at $X^{\mathrm{Am}}_{\mathrm{Prg}} = 0.5$ for Qtz = 0 in (Opx), and at $X^{\mathrm{Am}}_{\mathrm{Prg}} = 0.2$ and 0.5 for Ol = 0 and Opx = 0 in (Qtz). The different reaction configurations are listed in Table 2.

Zeroths may result from either simple or complex expressions. The locations of zeroths in one, two, or three dimensional space are obtained by setting the equation for the stoichiometric coefficient for a phase to zero and solving for one exchange parameter in terms of the others.

In the 5/1 system (Table 1), the zeroths are points (filled circles in Fig. 1) on reaction lines. Here stoichiometries depend on one compositional variable only. The points are positioned as follows:

for (Ol)	Cpx = 0	at $x = 2$	(outside the allowed composition space)
	Qtz = 0	at $x = 0.2$	
for (Opx)	Cpx = 0	at $x = 2$	(outside the allowed composition space)
	Qtz = 0	at $x = 0.5$	
for (Qtz)	Cpx = 0	at $x = 2$	(outside the allowed composition space)
	Opx = 0	at $x = 0.5$	
	Ol = 0	at $x = 0.2$.	

The different reaction configurations in relation to the amphibole composition are listed in Table 2 and are shown in Figure 1.

In the six component system, zeroths are dependent on x, y (and z). In the 6/2 multisystem, they are lines as shown in Figure 2. Three reaction squares (Qtz), (Opx), and (Ol) with corresponding lines for clinopyroxene, spinel, olivine, orthopyroxene, and quartz are displayed. Zero

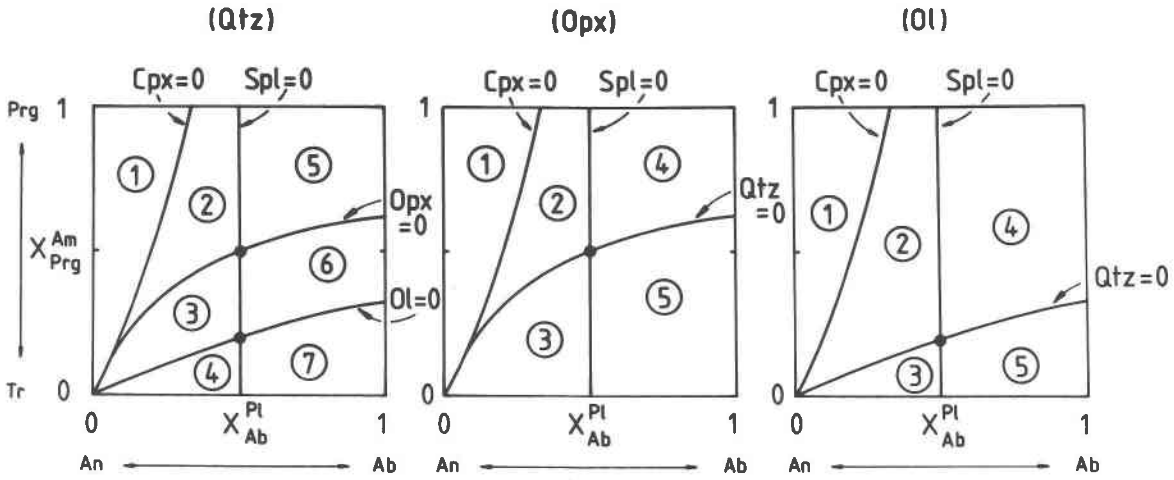

Fig. 2. Zeroths in the reaction squares defined by X^{Am}_{Prg} and X^{Pl}_{Ab}. The zero line Spl = 0 at X^{Pl}_{Ab} = 0.5 corresponds to the reaction line of Figure 1. The different reaction configurations are listed in Table 3.

lines can either be straight or curved. In the 6/3 multisystem, zeroths are surfaces in reaction cubes, as shown in Figure 3. The zeroths for indispensable phases are constant in the reaction space of a certain multisystem, whereas zeroths of substitutable phases vary. Zero points (in the 5/1 multisystem), lines (in the 6/2 multisystem), and surfaces (in the 6/3 multisystem) subdivide the reaction space (line, plane, cube) into different sections. Each section is characterized by a specific configuration of minerals on each side of a reaction equation. The different configurations for the 5/1, 6/2, and 6/3 multisystem are listed in Tables 2, 3, and 4, respectively.

Zero points, lines, and surfaces of substitutable phases may coincide. The points, lines, and surfaces where Ol = 0 and Opx = 0 in (Qtz) coincide with the zeroths of quartz in (Ol) and in (Opx), respectively. This coincidence can be explained by examining how mineral stoichiometries are determined. While plagioclase, diopside, spinel, and either enstatite or forsterite are used to solve for Na, Ca, Al, and Mg (or Fe), remaining Si is used to determine one of the stoichiometries of two of the three minerals, forsterite, enstatite, or quartz. Because all three minerals have one Si atom per formula unit, congruent zero lines result.

The 5/1 multisystem is a degeneracy of the 6/2 multisystem. This degeneracy is shown in Figures 2a–2c as vertical line Spl = 0 at $y = 0.5$ ($X^{Pl}_{Ab} = 0.5$) which corresponds with the lines shown in Figures 1a–1c. Along the line Spl = 0, zero points from the 5/1 multisystem are shown as filled circles. Normally zero points, lines, and surfaces are limiting cases where the phase rule is no longer applicable. This is not the case on the line Spl = 0, as the disappearance of the oxide is accompanied by the combination of Na_2O and Al_2O_3 to $NaAl_3O_5$ and therefore by a decrease in one component. The degree of freedom does not change.

The reaction squares of Figure 2 represent those sections of the cubes in Figure 3 where z or X^{Spl}_{Hc} equals 1.

Table 2. Reaction configurations in the 5/1 multisystem

Reaction space (Qtz)
(1) Am + Fo = Pl + Di + En + H_2O
(2) Am = Pl + Di + En + Fo + H_2O
(3) Am + En = Pl + Di + Fo + H_2O
Reaction space (Opx)*
(1) Am = Pl + Di + Fo + Qtz + H_2O
(2) Am + Qtz = Pl + Di + Fo + H_2O
Reaction space (Ol)**
(1) Am = Pl + Di + En + Qtz + H_2O
(2) Am + Qtz = Pl + Di + En + H_2O

* No zero point for Fo.
** No zero point for En.

Table 3. Reaction configurations in the 6/2 multisystem

Reaction space (Qtz)
(1) Am + Spl + Di + En = Pl + Fo + H_2O
(2) Am + Spl + En = Pl + Di + Fo + H_2O
(3) Am + Spl = Pl + Di + En + Fo + H_2O
(4) Am + Spl + Fo = Pl + Di + En + H_2O
(5) Am + En = Pl + Di + Spl + Fo + H_2O
(6) Am = Pl + Di + Spl + En + Fo + H_2O
(7) Am + Fo = Pl + Di + Spl + En + H_2O
Reaction space (Opx)*
(1) Am + Spl + Di + Qtz = Pl + Fo + H_2O
(2) Am + Spl + Qtz = Pl + Di + Fo + H_2O
(3) Am + Spl = Pl + Di + Qtz + Fo + H_2O
(4) Am + Qtz = Pl + Di + Spl + Fo + H_2O
(5) Am = Pl + Di + Spl + Qtz + Fo + H_2O
Reaction space (Ol)**
(1) Am + Spl + Di + Qtz = Pl + En + H_2O
(2) Am + Spl + Qtz = Pl + Di + En + H_2O
(3) Am + Spl = Pl + Di + Qtz + En + H_2O
(4) Am + Qtz = Pl + Di + Spl + En + H_2O
(5) Am = Pl + Di + Spl + Qtz + En + H_2O

* No zero line for Fo.
** No zero line for En.

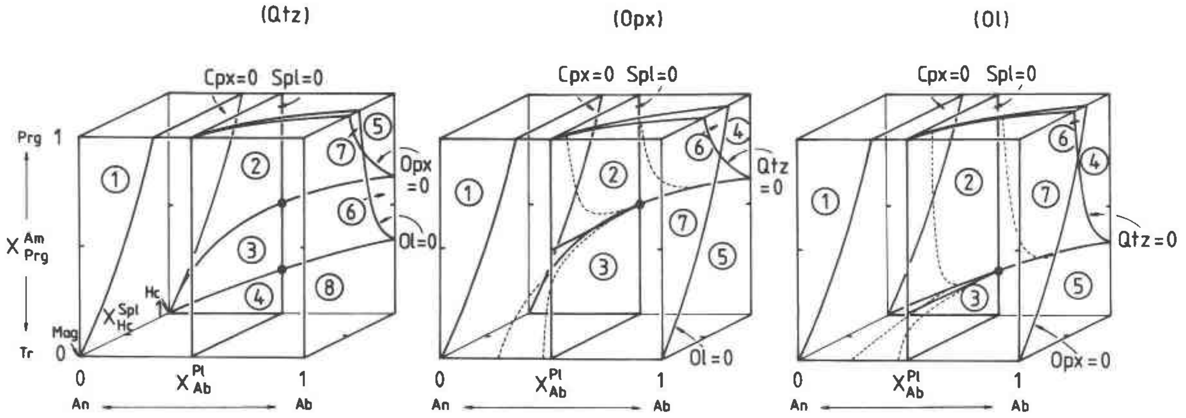

Fig. 3. Zeroths in the reaction cubes defined by X^{Am}_{Prg}, X^{Pl}_{Ab}, and X^{Spl}_{Hc}. The plane $X^{Spl}_{Hc} = 1.0$ corresponds to the reaction plane of Figure 2. The zero surfaces of Opx = 0 and Ol = 0 in (Qtz) and of Qtz = 0 in (Ol) and in (Opx), respectively, intersect the plane $X^{Pl}_{Ab} = 0.5$ at a fixed value of X^{Am}_{Prg} and are independent of the composition of spinel. For Ol = 0 in (Qtz) and Qtz = 0 in (Ol) the intersection is at $X^{Am}_{Prg} = 0.2$, for Opx = 0 in (Qtz), and Qtz = 0 in (Opx) the intersection is at $X^{Am}_{Prg} = 0.5$. The shape of the zero surfaces on either side of $0.5 > X^{Pl}_{Ab} > 0.5$ is indicated by dashed lines in Figures 3b and 3c. The different reaction configurations are listed in Table 4.

In the cubes of Figures 3b and 3c, the zero surfaces of olivine (Ol = 0) in (Opx) and orthopyroxene (Opx = 0) in (Ol) do not intersect the section where $z(X^{Spl}_{Hc}) = 1$ or $y(X^{Pl}_{Ab}) = 0.5$. This explains the absence of zero points and lines of Ol and Opx in Figures 1b and 1c as well as Figures 2b and 2c.

STABILITY RELATIONS

Schreinemakers rules are applicable as long as mineral compositions are fixed. Reaction bundles are most reasonably constructed where exchange parameters equal zero or one. Where stoichiometric coefficients are zero, reaction curves may coincide. In favorable cases, such degeneracies may help to construct a phase diagram for continuous reactions thereby putting constraints on the mixing properties of solid solutions. An example for the behavior of the Schreinemakers bundles at zeroths is the subject of the following discussion and will be discussed for the transition of the 4/0 to the 5/1 multisystem. A similar, but more complex, exercise could be done for the six component systems.

In the system containing four components, amphibole is pure tremolite ($x = 0$) and plagioclase is absent. The reactions (Ol), (Opx), and (Qtz) may be arranged in two different ways in a *P-T* grid. Either (Opx) is at the high *P-T* side and (Ol) and (Qtz) are in the low *P-T* region or vice versa. The Schreinemakers bundle, consistent with reaction slopes as calculated for the 4/0 system and using the database of Helgeson et al. (1978), is shown in Figure 4a. Temperature and fluid pressure were assumed to be 800 °C and 2 kbar, corresponding to the approximate upper stability limit of tremolite (Jenkins, 1983) at a specific fluid pressure. The tremolite field, established by the two tremolite dehydration reactions (Ol) and (Opx), encloses an angle smaller than 180°. The (Qtz) reaction is located in the tremolite stability field. Its metastable extension lies in the quartz stability field. Figure 4 only shows partial bundles, which explains the presence of angles exceeding 180°.

The introduction of $NaAl_3O_5$ to the four-component system results in the continuous incorporation of pargasite into tremolite and in the appearance of plagioclase ($X^{Pl}_{An} = 0.5$), the stoichiometry of which increases linearly with *x*. During the increase of *x*, zeroths are crossed at $x = 0.2$ and 0.5. The phase diagrams at $x = 0.2$, 0.5, and 1.0 are shown in Figures 4b–4d, respectively. The disappearance of minerals at $x = 0.2$ and 0.5 leads to the coincidence of reaction curves. At $x = 0.2$, these are the reactions (Qtz) and (Ol)

TABLE 4. Reaction configurations in the 6/3 multisystem

Reaction space (Qtz)
(1) Am + Spl + Hd + Fs = Pl + Fa + H_2O
(2) Am + Spl + Fs = Pl + Hd + Fa + H_2O
(3) Am + Spl = Pl + Hd + Fs + Fa + H_2O
(4) Am + Spl + Fa = Pl + Hd + Fs + H_2O
(5) Am + Fs = Pl + Hd + Spl + Fa + H_2O
(6) Am = Pl + Hd + Spl + Fs + Fa + H_2O
(7) Am + Fs + Fa = Pl + Hd + Spl + H_2O
(8) Am + Fa = Pl + Hd + Spl + Fs + H_2O
Reaction space (Opx)
(1) Am + Spl + Hd + Qtz = Pl + Fa + H_2O
(2) Am + Spl + Qtz = Pl + Hd + Fa + H_2O
(3) Am + Spl = Pl + Hd + Qtz + Fa + H_2O
(4) Am + Qtz = Pl + Hd + Spl + Fa + H_2O
(5) Am = Pl + Hd + Spl + Qtz + Fa + H_2O
(6) Am + Qtz + Fa = Pl + Hd + Spl + H_2O
(7) Am + Fa = Pl + Hd + Spl + Qtz + H_2O
Reaction space (Ol)
(1) Am + Spl + Hd + Qtz = Pl + Fs + H_2O
(2) Am + Spl + Qtz = Pl + Hd + Fs + H_2O
(3) Am + Spl = Pl + Hd + Qtz + Fs + H_2O
(4) Am + Qtz = Pl + Hd + Spl + Fs + H_2O
(5) Am = Pl + Hd + Spl + Qtz + Fs + H_2O
(6) Am + Qtz + Fs = Pl + Hd + Spl + H_2O
(7) Am + Fs = Pl + Hd + Spl + Qtz + H_2O

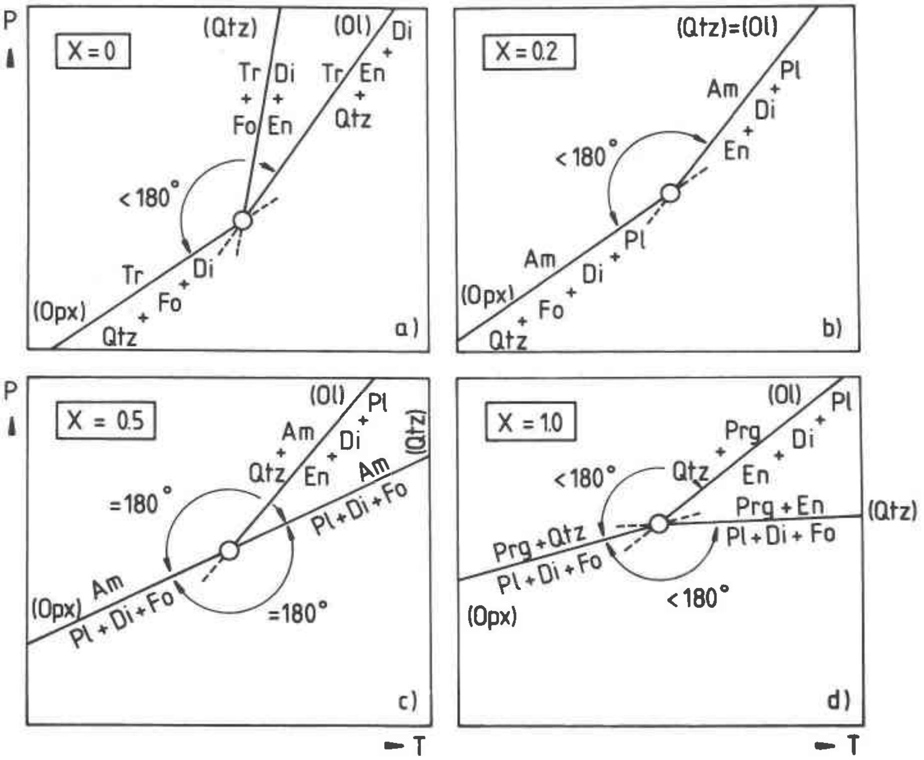

Fig. 4. Partial Schreinemakers bundles in the multisystem containing four and five components. The relative positions of reaction curves were determined by calculating the dP/dT slopes at 800 °C and 2 kbar for the two positions at $X^{\mathrm{Am}}_{\mathrm{Prg}} = 0$ and 1. Plagioclase in **a** is anorthite; plagioclase in **b** through **d** has an anorthite content of 50 mol%.

$$\text{(Qtz)}\quad 1.0\ \mathrm{Am}^{\mathrm{Prg}}_{0.2} = 0.4\mathrm{Pl}^{\mathrm{An}}_{0.5} + 1.8\mathrm{Di} + 3.0\mathrm{En} + 1.0\mathrm{H_2O} \qquad (13)$$

$$\text{(Ol)}\quad 1.0\ \mathrm{Am}^{\mathrm{Prg}}_{0.2} = 0.4\mathrm{Pl}^{\mathrm{An}}_{0.5} + 1.8\mathrm{Di} + 3.0\mathrm{En} + 1.0\mathrm{H_2O} \qquad (14)$$

because of the disappearance of quartz in (Ol) and of olivine in (Qtz). The amphibole stability field is enclosed by reactions forming an angle <180°.

At $x = 0.5$, enstatite in (Qtz) and quartz in (Opx) disappear. The reaction slopes of

$$\text{(Qtz)}\quad 1.0\ \mathrm{Am}^{\mathrm{Prg}}_{0.5} = 1.0\mathrm{Pl}^{\mathrm{An}}_{0.5} + 1.5\mathrm{Di} + 1.5\mathrm{Fo} + 1.0\mathrm{H_2O} \qquad (15)$$

$$\text{(Opx)}\quad 1.0\ \mathrm{Am}^{\mathrm{Prg}}_{0.5} = 1.0\mathrm{Pl}^{\mathrm{An}}_{0.5} + 1.5\mathrm{Di} + 1.5\mathrm{Fo} + 1.0\mathrm{H_2O} \qquad (16)$$

therefore coincide. In contrast to $x = 0.2$, the reaction curves extend on the metastable extension of each other. Both sides of Reactions 15 and 16 are characterized by the same minerals and stoichiometries, and thus both enclose an angle of 180°. This is not the case in Figure 4d where the stoichiometries of the minerals Pl, Di, and Fo in reactions (Qtz) and (Opx) differ. The angle is therefore smaller than 180°. In the new configuration of Figure 4d, amphibole is pure pargasite, and the bundle is consistent with the changes encountered from $x = 0$ to 0.2, 0.5, 1.0 and is consistent with Schreinemakers rules.

APPLICATION TO A MAFIC REPLACEMENT PEGMATITE OF THE BUSHVELD COMPLEX

The method described has been applied to a mafic replacement pegmatite from the Brits area of the Bushveld Complex (Fig. 5; Zingg, in preparation). Whole rock analyses display constant concentrations in $\mathrm{Na_2O}$, $\mathrm{Al_2O_3}$, and MgO and some variation in FeO, $\mathrm{Fe_2O_3}$, CaO, and $\mathrm{SiO_2}$ inside the pegmatite. A closed system is suggested by the complementary behavior in the variation of mineral compositions.

Whereas the modal ratio of calcic to sodic amphibole (Fig. 6) increases, electron microprobe analyses show that plagioclase becomes sodic (Fig. 7). Amphibole becomes more magnesian towards the pegmatite's center (Table 5), whereas olivine becomes more ferrous. The variation of divalent and trivalent Fe can be disregarded, as the model reaction will be derived for the Mg subsystem only. The following approach represents the limiting case for a closed system.

Petrography and geochemistry

The pegmatite is characterized in the field by its coarse grain size and transgressive character. It may be subdivided into three zones (Fig. 6). The boundary between border and transition zone has been defined where plagioclase for the first time drops below a composition of

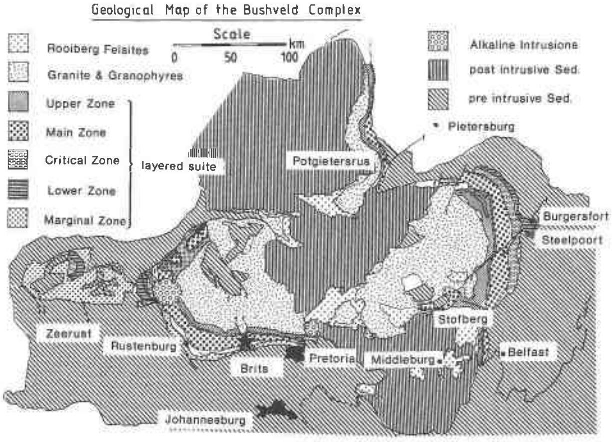

Fig. 5. Geological map of the Bushveld Complex (modified after Sacs, 1980). The pegmatite from which reactions were derived is from the Brits area.

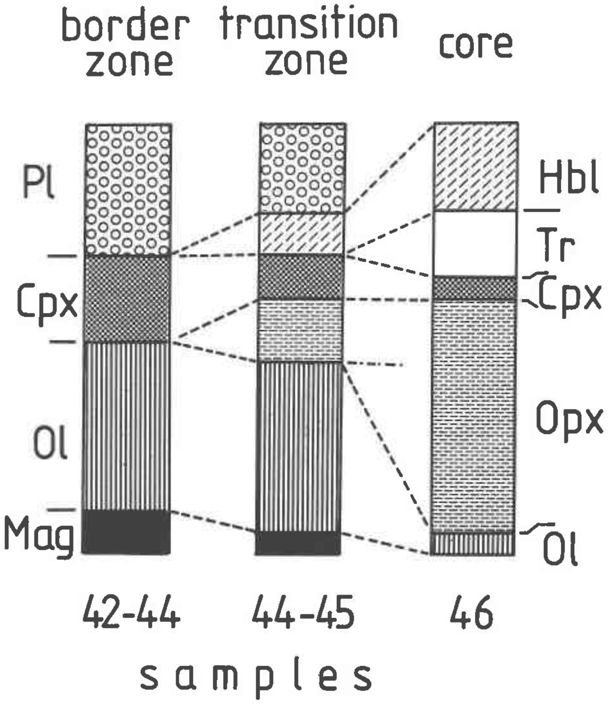

Fig. 6. Schematic diagram showing the variation of mineral proportions in a cross section of the pegmatite from border to center. The diagram is only qualitative, as the coarse grain size and the heterogeneity of the rock preclude a more quantitative determination of mineral proportions. The ratio of orthopyroxene to olivine varies in the transition zone.

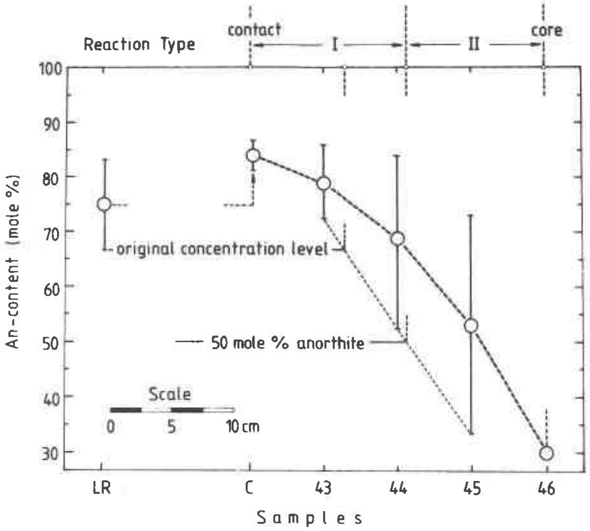

Fig. 7. Compositional variation of plagioclase across the pegmatite. Given are the average composition as well as the range. LR represents unaffected layered rock. Reaction types I and II refer to the two reaction segments encountered in the pegmatite's reaction space.

50% An (Fig. 7). This is the position where a zeroth is crossed.

The pegmatite's contact consists of olivine, clinopyroxene, coarse-grained plagioclase, and subordinate magnetite. In the border zone, olivine is surrounded by a fresh rim of orthopyroxene. Hornblende replaces plagioclase and clinopyroxene. From border to transition zone, feldspar, olivine, and clinopyroxene have decreased in abundance. The appearance of tremolite in the pegmatite's core is coupled with the complete disappearance of feldspar. Mineral reactions are witnessed by corona textures such as the overgrowth of orthopyroxene on olivine or hornblende surrounding clinopyroxene and plagioclase.

The decrease in plagioclase mode is accompanied by a decrease in the An content (Fig. 7). The figure shows the average composition as well as the range. Plagioclase at the contact has a composition of 85 (± 2) mol% An, whereas feldspar from unaffected host rock is more sodic ($X^{Pl}_{An} = 0.75$). In the border (zone I in Fig. 7) and transition zone (zone II in Fig. 7) the average An content decreases while the range increases. A small remnant of feldspar in sample 46 (core) has an An content of 30 mol%. In contrast to plagioclase, brown amphibole displays a fairly constant composition over the whole of the pegmatite (Fig. 8). Amphibole from the core however is zoned.

The zoning in amphibole enables the determination of exchange vectors (Zingg, in preparation). Magnesium tremolite was defined as the additive component, and the following principal vectors are distinguished: $FeMg_{-1}$, $NaAl\square_{-1}Si_{-1}$, $AlAlMg_{-1}Si_{-1}$, and $FeCa_{-1}$.

The ed and tk vectors occur in the same proportions. The $FeCa_{-1}$ exchange reaches a maximum mole fraction of 0.05 and will be neglected in the derivation of the reaction relationship. There is good evidence to suggest a low concentration of Fe^{3+}. Na is limited to the A-site and occurs in the ed vector only. It may therefore be used

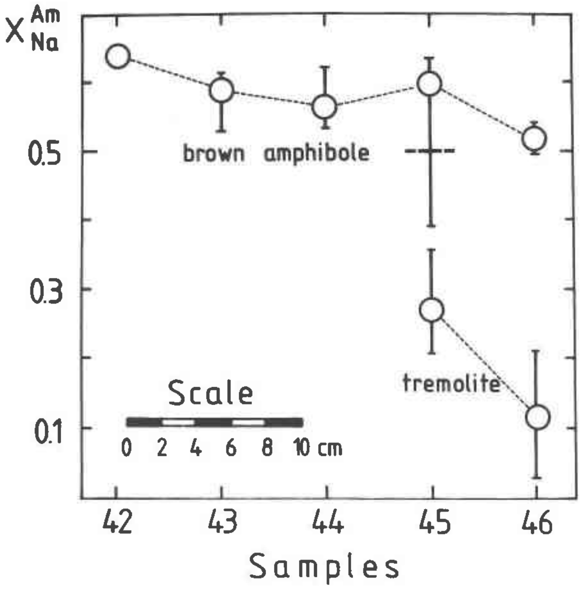

Fig. 8. Compositional variation of Na in the A-site of amphibole across the pegmatite. Given are the average composition as well as the range. In samples 45 and 46, brown amphibole coexists with tremolite.

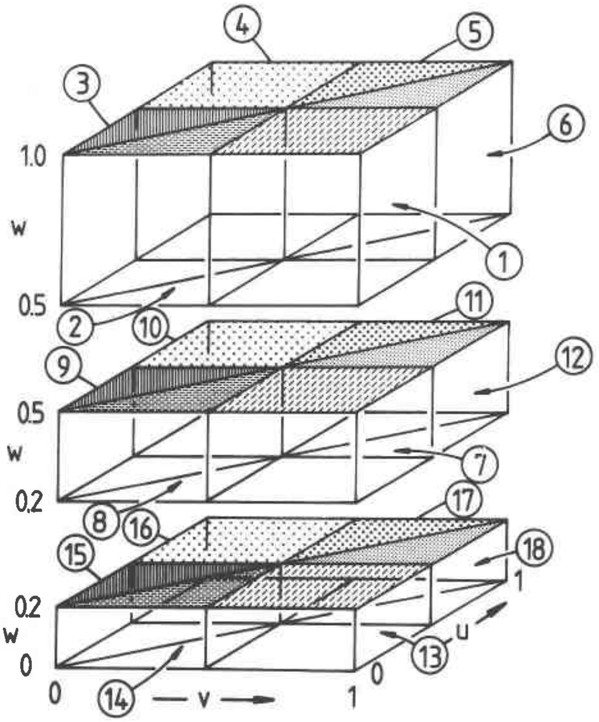

Fig. 9. Reaction space containing 18 different reactions. The cube has a twofold line on symmetry and each reaction has a counterpart of the opposite side of the central vertical axes. The nine different configurations are listed in Table 7.

to estimate the pargasite component which will be assumed to be 0.55 (Fig. 8).

Mineral reactions and reaction space

Minerals participating in the reaction are amphibole, plagioclase, clinopyroxene, orthopyroxene, and olivine. Sulphides, ilmenite, and biotite are present in subordinate amounts and will be disregarded. With the exception of spinel, all the ferromagnesian minerals are more magnesian than ferrous, and the reaction is written for the Mg end-members only. Consequently, spinel, an almost pure magnetite, is also disregarded. The mass balance between Mg end-members describes the reacting mineral phases in the correct proportions.

Among the reactions discussed so far, the one most suitable to describe the textural observations is Reaction 6. However, plagioclase in Reaction 6 has a fixed composition of 50 mol% An. This is not an acceptable explanation for what is observed in the pegmatite (Fig. 7). No other Al mineral is present, and pyroxene is low in jadeite and tschermak components. The problem imposed by the compositional variation in plagioclase is by-passed by introducing a second type of feldspar. It is proposed that Na, Ca, and Al are balanced between amphibole, a reactant, and product plagioclase, according to the equation

$$\begin{aligned}&\mathrm{Na}_w\mathrm{Ca}_2\mathrm{Mg}_{5-w}\mathrm{Al}_{3w}\mathrm{Si}_{8-2w}\mathrm{O}_{22}(\mathrm{OH})_2\\&\quad + a\mathrm{Na}_u\mathrm{Ca}_{1-u}\mathrm{Al}_{2-u}\mathrm{Si}_{2+u}\mathrm{O}_8\\&\quad = b\mathrm{Na}_v\mathrm{Ca}_{1-v}\mathrm{Al}_{2-v}\mathrm{Si}_{2+v}\mathrm{O}_8 + c\mathrm{CaMgSi}_2\mathrm{O}_6\\&\qquad + d\mathrm{MgSiO}_3 + e\mathrm{Mg}_2\mathrm{SiO}_4 + \mathrm{H}_2\mathrm{O}. \qquad (17)\end{aligned}$$

The stoichiometric coefficients of Reaction 17 are listed in Table 6 and the reaction cube is shown in Figure 9. Except for that of feldspar, stoichiometric coefficients are

TABLE 5. Electron microprobe analyses of zoned amphibole from sample 46 of the Brits Pegmatite*

	tremolitic ←							→	pargasitic
Si	7.76	7.57	7.44	7.34	6.95	6.79	6.78	6.52	6.51
$^{[4]}$Al	0.24	0.43	0.56	0.66	1.05	1.21	1.23	1.48	1.49
$^{[6]}$Al	0.17	0.26	0.33	0.36	0.42	0.46	0.47	0.46	0.51
Ti	0.01	0.03	0.04	0.06	0.12	0.16	0.16	0.29	0.27
Fe	1.17	1.26	1.40	1.45	1.52	1.54	1.54	1.66	1.70
Mn	0.02	0.02	0.02	0.03	0.02	0.02	0.01	0.02	0.02
Mg	3.76	3.52	3.26	3.14	2.97	2.91	2.83	2.61	2.56
Ca	1.84	1.86	1.88	1.88	1.89	1.87	1.87	1.86	1.85
Na	0.13	0.22	0.26	0.31	0.51	0.51	0.55	0.60	0.60

* Based on 23 O atoms.

TABLE 6. Reaction relationship in a pegmatite from the Brits area (Bushveld Complex)

Reaction equation

$Am(w) + aPl(u) = bPl(v) + cCpx + dOpx + eOl + H_2O$

Stoichiometric coefficients

$a = [w(2v - 1)]/(u - v)$, $b = [w(2u - 1)]/(u - v)$

$c = 2 - w$, $d = 5 - 10w$, $e = 5w - 1$

Zero positions

$Pl(u) = 0$ at $u = v$ and $v = 0.5$

$Pl(v) = 0$ at $u = v$ and $u = 0.5$

$Opx = 0$ at $w = 0.5$

$Ol = 0$ at $w = 0.2$

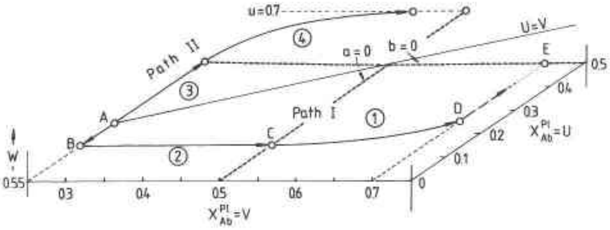

Fig. 10. Reaction path and segments at $w = 0.55$ and proposed for the Brits pegmatite. The reactions are

(1) $bPl(v) + cCpx + eOl + H_2O = Am(w) + aPl(u) + dOpx$

(2) $aPl(u) + bPl(v) + cCpx + eOl + H_2O = Am(w) + dOpx$.

The stoichiometries of ferromagnesian minerals only depend on w. The coefficients of plagioclase vary from point A ($a = \infty$, $b = \infty$) to point B ($a = 2.75$, $b = 3.85$) to C ($a = 0$, $b = 1.1$) to D ($a = -0.49$, $b = 0.61$) to E ($a = -1.1$, $b = 0$). The reaction is stopped on the line D-E. The details are given in the text.

the same as in Reaction 6. Zeroths exist at the following five positions: at $u = v$, at u or $v = 0.5$, and at $w = 0.2$ and 0.5. Eighteen reactions are distinguished by crossing the zero planes (Table 7). These are arranged in groups of six reactions at three different levels of w: a first level between $0 < w < 0.2$, a second between $0.2 < w < 0.5$, and a third between $0.5 < w < 1.0$. The reaction cube has a twofold line of symmetry and each reaction has an equivalent counterpart on the other side of the line. Consequently, from the 18 original reactions there are only 9 different phase configurations.

Because of symmetry reasons, two reaction paths are possible and shown in Figure 10. Only path I will be discussed. The figure displays the plane $w = 0.55$ of the reaction cube. Along path I, the zero plane $v = 0.5$ is crossed at point C and two reaction segments (2) and (1) are encountered:

$$\text{(2)}\quad bPl(v) + cDi + eFo + H_2O = Am(w) + aPl(u) + dEn \tag{18}$$

$$\text{(1)}\quad aPl(u) + bPl(v) + cDi + eFo + H_2O = Am(w) + dEn. \tag{19}$$

With the first trace of amphibole (with composition $w = 0.55$), the reaction is expected to start near the line $u = v$ at point A (Fig. 10) with the immediate production of calcic plagioclase. The stoichiometric coefficients of plagioclase on the line $u = v$ are infinite. Calcic plagioclase is produced until the reactant feldspar reaches a composition of 50 mol% An (point C in Fig. 10). Between points B and C, the stoichiometric coefficients of reactant (b) and product (a) feldspar decreases from 3.85 and 2.75 to 1.1 and 0, respectively. Plagioclase of composition u now changes its status in the equation and starts to be consumed in segment (1). In this reaction segment, the stoichiometries of a and b show a complementary behavior. Because the difference remains constant (i.e., $b - a = 2w$), $|a|$ increases from zero at C to 1.1 at E, whereas $|b|$ decreases from 1.1 at C to zero at E. This process is stopped on the line D-E with the disappearance of plagioclase of composition u, most probably where u is still smaller than 0.5. If $u > 0.5$, a new reaction segment would require the production of sodic plagioclase and in consequence its modal increase. This is not observed. The appearance of tremolite, coexisting with brown amphi-

TABLE 7. Reaction configurations in the reaction space of the Brits Pegmatite

	$1.0 > w > 0.5$
(1)	$Am(w) + dEn = aPl(u) + bPl(v) + cDi + eFo + H_2O$
(2)	$Am(w) + aPl(u) + dEn = bPl(v) + cDi + eFo + H_2O$
(3)	$Am(w) + bPl(v) + dEn = aPl(u) + cDi + eFo + H_2O$
(4) = (1)	$Am(w) + dEn = aPl(u) + bPl(v) + cDi + eFo + H_2O$
(5) = (2)	$Am(w) + aPl(u) + dEn = bPl(v) + cDi + eFo + H_2O$
(6) = (3)	$Am(w) + bPl(v) + dEn = aPl(u) + cDi + eFo + H_2O$
	$0.5 > w > 0.2$
(7)	$Am(w) = aPl(u) + bPl(v) + cDi + dEn + eFo + H_2O$
(8)	$Am(w) + aPl(u) = bPl(v) + cDi + dEn + eFo + H_2O$
(9)	$Am(w) + bPl(v) = aPl(u) + cDi + dEn + eFo + H_2O$
(10) = (7)	$Am(w) = aPl(u) + bPl(v) + cDi + dEn + eFo + H_2O$
(11) = (8)	$Am(w) + aPl(u) = bPl(v) + cDi + dEn + eFo + H_2O$
(12) = (9)	$Am(w) + bPl(v) = aPl(u) + cDi + dEn + eFo + H_2O$
	$0.2 > w > 0$
(13)	$Am(w) + eFo = aPl(u) + bPl(v) + cDi + dEn + H_2O$
(14)	$Am(w) + aPl(u) + eFo = bPl(v) + cDi + dEn + H_2O$
(15)	$Am(w) + bPl(v) + eFo = aPl(u) + cDi + dEn + H_2O$
(16) = (13)	$Am(w) + eFo = aPl(u) + bPl(v) + cDi + dEn + H_2O$
(17) = (14)	$Am(w) + aPl(u) + eFo = bPl(v) + cDi + dEn + H_2O$
(18) = (15)	$Am(w) + bPl(v) + eFo = aPl(u) + cDi + dEn + H_2O$

bole and coupled with the complete disappearance of feldspar, requires the formulation of a new reaction equation, containing two different amphibole compositions and no feldspar.

CONCLUSION

The method proposed in this study allows the derivation of reactions including end-member and solid solution minerals. The development from simple to complex systems may help to explain the role of the single participants in the reaction equation, in particular the role of indispensable and substitutable phases. The distinction between these types of phases has been shown to be of importance with respect to stoichiometric and to zeroths in reaction space. It seems evident that the equation should be normalized on that mineral which is not expected to change its status in the reaction equation.

The derivation of the proper reaction in a petrographic study is an important step and can be a study of its own. It is the step toward a more quantitative approach, as the physical chemical modeling is always based on reaction relationships. The inclusion of solid solutions requires the knowledge of mixing parameters. It is expected that such parameters may be obtained from experimental studies using the present model. Where mixing parameters are known, isotherms and isobars in the reaction space and, therefore, the formation conditions of a specific rock system can be modeled.

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