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CONTINUOUS REACTIONS IN THE $MgO–FeO–SiO_2–H_2O$ MULTISYSTEM

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ABSTRACT

Continuous reactions are derived for the quaternary multisystem MgO – FeO – SiO_2 – H_2O using the phases serpentine, talc, brucite, olivine, orthopyroxene and H_2O. Stoichiometric coefficients are expressed in terms of mole fractions and, if set equal to zero, define the position where a mineral changes from being produced to being consumed. "Zero contours" may be displayed graphically in reaction space, defined by the coordinate system with axes given by mole fractions. Zero contours in Mg–Fe systems have characteristic features. They have a linear geometry, *i.e.*, they are lines in two-dimensional space, planes in three-dimensional space. In the absence of pure end-member phases, all zero contours intersect the two corners (0,0,....) [= Fe-corner] and (1,1,....) [= Mg-corner] of reaction (hyper-)space. The line connecting the two corners is the location where all zero contours intersect, and where no reaction is possible. In the presence of a pure phase, the zero contour of the pure phase intersects that corner of reaction space with which it is not compatible. No other zero contour may intersect that corner. The disappearance of a phase at the corner parallels the disappearance of a component, leaving the system univariant. A reaction is still possible. In the presence of two serpentine minerals, two types of zero contours are distinguished. Where the composition of the two serpentine minerals coincides, all phases except serpentine disappear. The zero contours of the two serpentine minerals are complementary to each other. Each of the two depends on the composition of coexisting non-serpentine minerals as well as on the composition of the other serpentine. The technique is applied to serpentinization in Bushveld layered rocks in South Africa.

Keywords: continuous reaction, exchange vector, reaction space, chemography, serpentine, antigorite, lizardite, chrysotile, greenalite, talc, minnesotaite, brucite, Bushveld, South Africa.

SOMMAIRE

Des réactions continues ont été dérivées pour le système quaternaire MgO – FeO – SiO_2 – H_2O en utilisant les phases serpentine, talc, brucite, olivine, orthopyroxène et H_2O. Les coefficients stoechiométriques sont exprimés en termes de fractions molaires. Si ceux-ci sont mises égales à zéro, elles définissent la transition de l'état de produit à l'état de réactif. De tels "contours zéro" peuvent être exprimés graphiquement dans l'espace réactionnel, tel que défini par un système de coordonnées ayant comme axes les fractions molaires. Dans les systèmes Mg–Fe, les contours zéro possèdent les caractéristiques suivantes: ils ont une géométrie linéaire, et donc constituent des lignes en deux dimensions, des plans en trois dimensions, *etc.* En l'absence de phases correspondant aux pôles purs, tous les contours zéro recoupent les deux coins (0,0,....) [coin Fe] et (1,1,....) [coin Mg] de l'espace (ou l'hyper-espace) réactionnel. La ligne entre les deux coins contient tous les contours zéro, et marque la condition où aucune réaction n'est possible. En présence d'une phase pure, le contour zéro de cette phase recoupe le coin de l'espace réactionnel avec lequel il n'est pas compatible. Aucun autre contour zéro ne peut recouper ce coin. La disparition d'une phase à ce coin accompagne l'élimination d'une composante du système, ce qui rend le système univariant. Une réaction est toujours possible. En présence de deux minéraux du groupe de la serpentine, il faut distinguer deux types de contours zéro. Où la composition de ces deux minéraux coïncide, toutes les phases exceptée la serpentine disparaissent. Les contours zéro des deux minéraux du groupe de la serpentine sont complémentaires. Chacun des deux dépend de la composition des phases coexistantes autres que la serpentine, ainsi que de la composition de la deuxième serpentine. La technique sert à analyser la serpentinisation des roches du complexe stratiforme du Bushveld, en Afrique du Sud.

(Traduit par la Rédaction)

Mots-clés: réaction continue, vecteur d'échange, espace réactionnel, chimiographie, serpentine, antigorite, lizardite, chrysotile, greenalite, talc, minnesotaïte, brucite, complexe du Bushveld, Afrique du Sud.

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INTRODUCTION

Reactions including serpentine minerals have been investigated in Mg-bearing multisystems, a ternary one containing $MgO–SiO_2–_2O$ (Evans *et al.* 1976, O'Hanley 1987), and the quaternary systems of $CaO–MgO–SiO_2–H_2O$ (Oterdoom 1978) and $Al_2O_3–MgO–SiO_2–H_2O$ (Caruso & Chernosky 1979, O'Hanley *et al.* 1989). Two systems including Fe have been discussed by Frost (1985): a four-component system, Fe–Si–H–O, with the phases greenalite, grunerite, minnesotaite, fayalite, magnetite, quartz and iron, and one with the five components, Fe–Mg–Si–H–O.

Evans *et al.* (1976) studied the relationship among the six phases antigorite, chrysotile, brucite, talc, forsterite and H_2O. O'Hanley (1987) extended this assemblage by adding lizardite and enstatite. The quaternary system of Oterdoom (1978) includes the Ca-bearing phases tremolite and diopside. In the multisystem containing Al_2O_3 (Caruso & Chernosky 1979), the assemblage consists of antigorite, aluminous lizardite, clinochlore, talc, brucite, olivine and H_2O. O'Hanley *et al.* (1989) included chrysotile as well as the other phases in this system. The introduction of Fe^{2+} to a system containing magnesium has one major effect; it stabilizes olivine and quartz in favor of orthopyroxene (Frost 1985). The derivation of phase equilibria in the latter is only possible with a fixed ratio of Mg to Fe.

The aim of the present study is to derive continuous reactions for the serpentine multisystem $MgO–FeO–SiO_2–H_2O$. Silicates are no longer of fixed composition, but solid solutions of their Fe and Mg end-members. The exchange vector $FeMg_{-1}$ (Thompson 1982b, Burt 1988), applied to all the ferromagnesian minerals, will be converted to mole fractions. Mole fractions in turn are the basis for reaction space. A brief comparison with the approach of Thompson (1982a, b) is given in the next section.

The study is a first application of a newly developed technique (Zingg 1991, 1992) to a system containing only one exchange vector, $FeMg_{-1}$. The purpose of the study is primarily to derive the rules governing reactions including Fe–Mg solid solutions. Serpentine multisystems are chemically among the simplest, and it seems reasonable to apply the vector $FeMg_{-1}$ to the ternary system $MgO–SiO_2–H_2O$.

The paper is subdivided into two parts. In the first part, nine reaction systems are derived: four include one serpentine, and the other five include two serpentine minerals. In the second part, the method is extended and applied to an open system, including aqueous species. An example of the latter approach is given for serpentinization in the Bushveld Complex.

THE TECHNIQUE

The application of exchange vectors to mineral systems is due to Thompson (1982a, b, Thompson *et al.* 1982) and involves two steps. In a first step, minerals and their compositional variation are defined and graphically displayed in composition space (Thompson 1982a). This is accomplished in terms of additive components and exchange vectors. In a second step, the actual reaction is written, including the additive components and exchange vectors. Each reaction is assigned a progress variable (Prigogine & Defay 1954). Reaction space records the molar amount of each phase transformed according to the progress variable $\Delta\xi_r$. The physically accessible part of reaction space is defined by a polytope in *n*-dimensional space.

In the method used below, the duality between composition and reaction space no longer exists. This is made possible by redefining solid solutions. The exchange vectors of Thompson are converted to mole fractions. Instead of writing a Fo + x $FeMg_{-1}$ to describe solid solution between forsterite and fayalite, the mineral formula $a\ (Mg_xFe_{1-x})_2SiO_4$ is introduced. Stoichiometric coefficients are expressed and vary as a function of mole fractions. If stoichiometric coefficients, which are dependent on mole fractions, become zero

$$a = 0 = f(x,y,z),$$

the mineral disappears from the equation (not necessarily from the mineral assemblage). This is the condition where a mineral changes from being produced to being consumed and *vice versa*. The *zero contour* (Fisher 1990) can be obtained as an analytical expression by setting the stoichiometric coefficient equal to zero and by solving in terms of one of the mole fractions:

$$x = f(y,z).$$

If reaction space is defined by the coordinate system of mole fractions (x,y,z), the zero contour for each mineral can be displayed graphically. In systems with one solid-solution mineral, reaction space is a line, and the zero contour is a point (Zingg 1991); with two solid-solution minerals, reaction space is a square, and zero contours are straight and curved lines; with three solid-solution minerals, reaction space is a cube, and zero contours are planes and surfaces, and with four and more solid-solution minerals, the reaction space is a hyperspace. Zero contours are the prime element in the present approach. They subdivide reaction space into different segments, in which a mineral has either a positive or negative stoichiometry. Each segment gives one possible configuration of minerals in a reaction equation. Crossing a zero contour results in a new configuration. The fact that reaction space is defined by mole fractions, which vary between 0 and 1, makes the whole reaction-space physically accessible. In Thompson's approach, the physically accessible part of reaction space, the polytope, has to be determined specifically from case to case. The

TABLE 1. NOMENCLATURE

Multisystem : System where $P > C + 1$ (P = No. of phases, C = No. of components)

Indispensable Phase : Phase which cannot be removed in a univariant reaction without degenerating the multisystem

Substitutable Phase : Phase which can be removed in a univariant reaction without degenerating the multisystem

Reaction Line : Reaction space in a system with one solid-solution mineral

Reaction Square : Reaction space in a system with two solid-solution minerals

Reaction Cube : Reaction space in a system with three solid-solution minerals

Reaction Hyperspace : Reaction space in a system with more than three solid-solution minerals

Reaction Subspace : Reaction space defined by less than the maximum number of mole fractions contained in a system. Reaction hyperspace can only be displayed graphically in reaction subspace.

Zero-Point : Position where the stoichiometry of a phase changes sign in one-dimensional reaction space

Zero-Line: Position where the stoichiometry of a phase changes sign in two-dimensional reaction space

Zero-Plane: Position where the stoichiometry of a phase changes sign in three-dimensional reaction space

Zero Contour : General term in n-dimensional reaction space ($n>0$), where the stoichiometry of a phase changes sign in a reaction equation (term suggested by Fisher 1990)

Reaction Segment : Line, area or volume portion in reaction space which is bounded by zero contours and which is characterized by one specific reaction configuration

Reaction Configuration : one way of arranging reactants and products in an equation. The compositional limits of a reaction configuration are defined in space by a reaction segment

Reaction System : entity of stoichiometrically, infinitesimally different reactions contained in a specific reaction space.

First-Order Degeneracy : disappearance of one phase at zero contour is accompanied by disappearance of one component leaving the system univariant.

Second-Order Degeneracy : disappearance of two phases at coinciding zero contours is accompanied by disappearance of two components leaving the system univariant

nth Order Degeneracy : disappearance of n phases at coinciding zero contours is accompanied by disappearance of n components leaving the system univariant

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different ways minerals are arranged (as reactants and products) in a reaction equation are called *reaction configurations* (Table 1).

The present technique is not concerned with stability relations, as it is purely algebraic. The thermodynamics of continuous reactions may be part of a second stage. A main precondition for this second step is the knowledge of mixing parameters. In order to comply with the nomenclature of Zen (1966), reactions are labeled by listing the absent phase(s) in *parentheses* [*e.g.*, (Ol)]. The zero contour of a phase is labeled by *braces* [*e.g.*, {Ol}]. Invariant points are given by *brackets* (*e.g.*, [Ol]: Cheng & Greenwood 1990). Minerals are represented by the abbreviations recommended by Kretz (1983). The terms used in the study are defined in Table 1.

THE SYSTEM

The system investigated is one of the simplest possible, chemically, and contains the four components

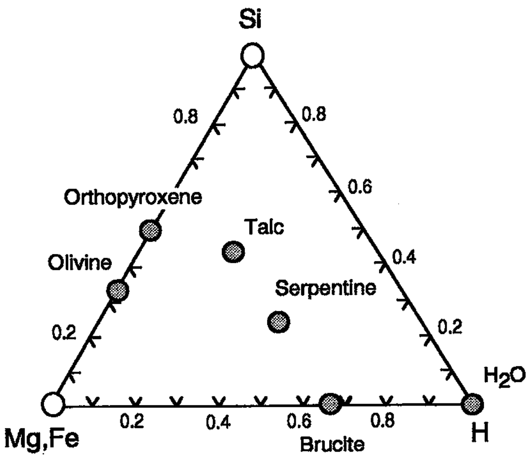

FIG. 1. Chemography of the system Si – Mg,Fe – H, including talc, orthopyroxene, serpentine, olivine, brucite and H_2O.

TABLE 2. PHASES, FORMULAS, ABBREVIATIONS AND MOLE FRACTIONS

Phase	Abbreviation [1]	Formula	Mole fractions
Serpentine	Srp	$(Mg_xFe_{1-x})_3Si_2O_5(OH)_4$	$x,y,z = X^{Srp}_{Mg}$
Antigorite	Atg		
Lizardite	Lz	$Mg_3Si_2O_5(OH)_4$	$X^{Srp}_{Mg} = 1$
Chrysotile	Ctl		
Greenalite	Gre	$Fe_3Si_2O_5(OH)_4$	$X^{Srp}_{Mg} = 0$
Talc	Tlc	$(Mg_uFe_{1-u})_3Si_4O_{10}(OH)_2$	$u = X^{Tlc}_{Mg}$
Talc	Tlc	$Mg_3Si_4O_{10}(OH)_2$	$X^{Tlc}_{Mg} = 1$
Minnesotaite	Min	$Fe_3Si_4O_{10}(OH)_2$	$X^{Tlc}_{Mg} = 0$
Orthopyroxene	Opx	$Mg_vFe_{1-v}SiO_3$	$v = X^{Opx}_{Mg}$
Enstatite	En	$MgSiO_3$	$X^{Opx}_{Mg} = 1$
Ferrosilite	Fs	$FeSiO_3$	$X^{Opx}_{Mg} = 0$
Olivine	Ol	$(Mg_wFe_{1-w})_2SiO_4$	$w = X^{Ol}_{Mg}$
Forsterite	Fo	Mg_2SiO_4	$X^{Ol}_{Mg} = 1$
Fayalite	Fa	Fe_2SiO_4	$X^{Ol}_{Mg} = 0$
Brucite	Brc	$(Mg_tFe_{1-t})(OH)_2$	$t = X^{Brc}_{Mg}$
Brucite	Brc	$Mg(OH)_2$	$X^{Brc}_{Mg} = 1$
Ferro-brucite	Fe-Brc	$Fe(OH)_2$	$X^{Brc}_{Mg} = 0$
Fluid	H_2O	H_2O	

[1] Mineral abbreviations after Kretz (1983)

$MgO–FeO–SiO_2–H_2O$. Five phases are required to form a univariant reaction [$P(H_2O) = P_{tot}$]. The chemography used is summarized in Figure 1 and includes the phases listed in Table 2.

Trivalent iron is not part of the system. This omission is made despite the fact that magnetite is a ubiquitous phase in serpentinized rocks (*e.g.*, Coleman & Keith 1971, Dungan 1979), and that antigorite, lizardite and chrysotile may incorporate variable amounts of Fe^{3+} (Whittaker & Wicks 1969, O'Hanley & Dyar 1993). The addition of trivalent iron would increase the system's complexity, and the reaction space could only be displayed graphically with simplifications. It is a prime purpose of this study to derive the rules governing reactions including the exchange vector $FeMg_{-1}$. It is the intention to develop a simple system as the basis for more complex ones, including other components in a next step. In order to apply real systems to the ones derived in this study, the ratio of divalent to trivalent iron has to be known, and only the Fe^{2+} part in a mineral phase should be considered.

The crystal chemistry of the serpentine minerals has been explored in studies by Wicks & Plant (1979), Wicks & Whittaker (1977) and in the excellent summary by Wicks & O'Hanley (1988). The main two elements in the crystal structure are an ideal magnesium-occupied sheet of octahedra and an ideal silicon-occupied sheet of tetrahedra. The lateral dimensions of the two sheets are different, and the misfit is responsible for the different structures of antigorite, lizardite and chrysotile. Serpentine minerals, in particular lizardite, contain some Al. Al^{3+} can be replaced by Fe^{3+} on both octahedral and tetrahedral sites (O'Hanley & Dyar 1993). Both Al^{3+} and Fe^{3+} relieve the misfit between sheets, even if Mg is partly replaced by Fe^{2+}. The compositional limits where lizardite transforms to the greenalite structure are not known (Guggenheim & Eggleton 1988), nor are the details on the exchange vector (O'Hanley, pers. comm., 1992).

In the present study, serpentine is assigned the formula $M_3Si_2O_5(OH)_4$ (where M represents Mg or Fe, or both). Antigorite was shown to deviate from the formula (Mellini *et al.* 1987), even in the absence of Fe^{3+} and Al^{3+}. The deviation is small (Mellini *et al.* 1987, Fig. 2) and will be neglected. Two types of reactions are distinguished, those including one serpentine mineral, presumably antigorite ("prograde"), and those including two serpentine minerals, presumably lizardite and chrysotile ("retrograde"). The only difference allowed between serpentine minerals is in the ratio Mg/(Mg+Fe). Brucite is strictly defined as $Mg(OH)_2$. In Deer *et al.* (1974), the Fe end-member $Fe(OH)_2$ is referred to as "ferro-brucite", which is the term used below. The solid solution will also be called brucite, except in cases where there could be confusion between the two terms. In the latter case, the solid solution will be referred to as brucite$_{ss}$.

Stoichiometric coefficients and reaction space were derived for the following systems: 1) four, including one polymorph of serpentine: (Tlc), (Brc), (Opx), (Ol); 2) five, including two polymorphs of serpentine: (Tlc, Brc), (Tlc, Opx), (Tlc, Ol), (Brc, Ol), (Brc, Opx).

The list does not include all possible combinations. Reactions without serpentine (Srp_1, Srp_2) or excluding both olivine *and* orthopyroxene (Opx, Ol), have been disregarded. This is because the study is concerned with serpentinization reactions, and most occurrences report on coexisting serpentine and either of olivine or orthopyroxene.

To keep each reaction as general as possible, the respective stoichiometric coefficients are expressed in terms of the mole fractions t, u, v, w and x/y (*e.g.*, Table 2). The actual reaction in a rock system can be evaluated by inserting compositions of real minerals, provided the assumptions are met (*i.e.*, closed system, absence of Fe^{3+}). An extension to open systems will be given as an application in the second part of this study.

In natural systems, mole fractions are not independent variables; they are coupled *via* distribution coefficients (*e.g.*, Trommsdorff & Evans 1972). Distribution coefficients are a reflection of partition energies between coexisting minerals. As the present technique is purely algebraic, they will be disregarded.

REACTION SYSTEMS INCLUDING ONE SERPENTINE MINERAL

Four reaction systems including one serpentine mineral are distinguished. These are (Tlc), (Brc), (Opx) and (Ol). The equations and stoichiometries are summarized in Table 3.

TABLE 3. REACTION SYSTEMS INCLUDING ONE SERPENTINE POLYMORPH

Reaction System (Tlc)

$$Srp_z = a\,Opx_v + b\,Ol_w + c\,Brc_t + d\,H_2O$$

$$a = \frac{4w-3z-t}{2w-v-t},\ b = \frac{3z-2v-t}{2w-v-t},\ c = \frac{2w-3z+v}{2w-v-t},\ d = \frac{2w-3v+3z-2t}{2w-v-t}$$

Reaction System (Brc)

$$Srp_z = a\,Opx_v + b\,Ol_w + c\,Tlc_u + d\,H_2O$$

$$a = \frac{12w+3u-15z}{2w+3u-5v},\ b = \frac{3(u+z-2v)}{2w+3u-5v},\ c = \frac{3z-v-2w}{2(2w+3u-5v)},\ d = \frac{3(2w+2u-3v-z)}{2w+3u-5v}$$

Reaction System (Opx)

$$Srp_z = a\,Ol_w + b\,Brc_t + c\,Tlc_u + d\,H_2O$$

$$a = \frac{6(t+u-2z)}{5+3u-8w},\ b = \frac{15z-12w-3u}{5+3u-8w},\ c = \frac{3z-4w+t}{2(5+3u-8w)},\ d = \frac{9(t+u-2z)}{5+3u-8w}$$

Reaction System (Ol)

$$Srp_z = a\,Opx_v + b\,Tlc_u + c\,Brc_t + d\,H_2O$$

$$a = \frac{6(t+u-2z)}{3u-4v+t},\ b = \frac{3z-2v-t}{2(3u-4v+t)},\ c = \frac{3(u+z-2v)}{3u-4v+t},\ d = \frac{3(t+u-2z)}{3u-4v+t}$$

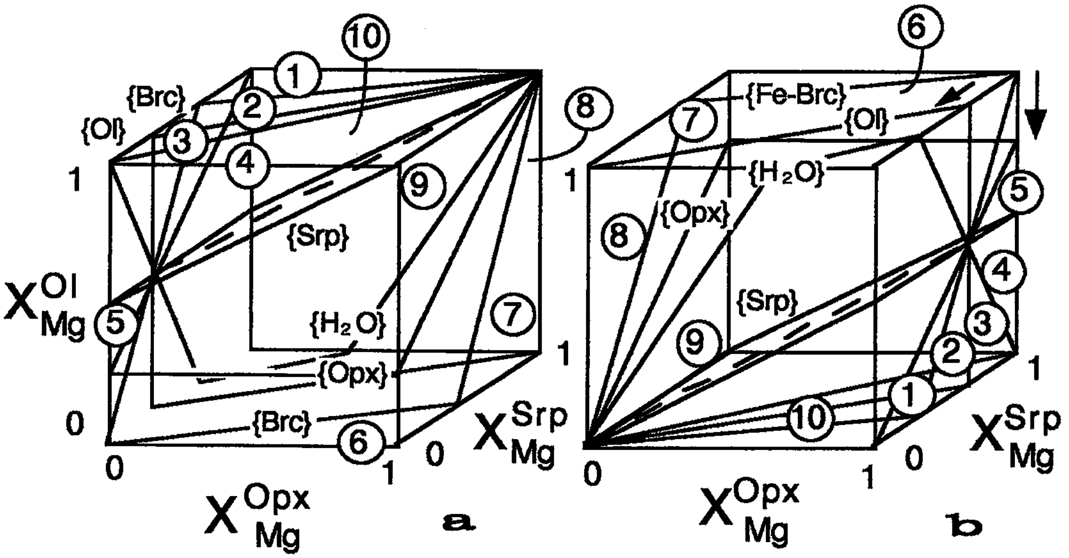

FIG. 2. Reaction subspaces for the system (Tlc). Fig. 2a displays five zero planes with brucite as $Mg(OH)_2$; Fig. 2b displays five zero planes with brucite as $Fe(OH)_2$. The zero planes record the location in reaction space, given by the mole fractions of X^{Ol}_{Mg}, X^{Opx}_{Mg} and X^{Srp}_{Mg}, where any of the phases brucite, serpentine, orthopyroxene, olivine and H_2O change their side in the equation. The arrows in b) record the shift of planes due to the change in brucite composition. Each cube can be derived from the other by a centrosymmetric inversion. The different reaction-configurations are listed in Table 4.

Reaction system (Tlc)

This system includes, and stoichiometric coefficients depend on, four mole fractions. The reaction space has four dimensions (*i.e.*, hyperspace) and cannot be displayed graphically without simplifications. The derivation of reaction configurations is not straightforward in the absence of reaction space. There are two ways to proceed. First, it is possible to hold one of the four mole fractions fixed (*e.g.*, "t" = 0 or 1 for brucite) and to construct a three-dimensional reaction subspace with the remaining three mole fractions (Fig. 2). This approach allows one to plot all the zero contours into the same cube, and configurations can be derived. In the second approach, the configurations are obtained *via* chemographic means.

The reaction subspace for end-member brucite, $Mg(OH)_2$, is shown in Figure 2a. The figure shows five independent zero contours, all of which are planes. The zero planes of the solid phases serpentine, brucite, orthopyroxene and olivine depend only on the mole fractions of coexisting minerals and not on their own compositions. The zero plane of H_2O in turn depends on all four mole fractions. All the zero planes intersect the Mg-corner (1,1,1) of reaction space. At this corner, iron is absent, and the system contracts to the ternary system $MgO–SiO_2–H_2O$. Which of the five phases (Srp, Brc, Ol, Opx, H_2O) has to be dropped is arbitrary; a reaction including all five phases is not possible. The origin (0,0,0) is only intersected by {Brc}. At (0,0,0), the system contracts to the ternary system $FeO–SiO_2–H_2O$, and brucite, which was defined before as $Mg(OH)_2$ and is the only phase containing Mg, is incompatible. It has to disappear. In contrast to the (1,1,1) corner, where no reaction was possible, the simultaneous disappearance of a component [Mg] and a phase [Brc] at (0,0,0) leaves the system univariant. The reaction is

$$\text{Gre} = \text{Fs} + \text{Fa} + 2\,H_2O.$$

Two zero planes intersect along a line. The disappearance of two phases along the line of intersection leaves the system overdetermined. As a result, no reaction is possible, and the remaining zero planes have to intersect the line as well. The line of intersection is the rotation axis along which each of the five zero planes can be derived from any other zero plane by rotation.

The zero planes subdivide the reaction cubes into different segments. A single plane cuts the cube into two segments. The fact that all five planes intersect along a rotation axis, and that each zero plane is crossed twice in a rotation of 360°, allow for ten different reaction-segments. They are numbered 1 to 10 in Figure 2 and are listed in Table 4. The fact that each zero plane in a 360° rotation is crossed twice and in a given sequence [reactions 1 → 5: sequence of zero

TABLE 4. REACTION CONFIGURATIONS IN THE REACTION SYSTEMS (TLC), (BRC), (OPX) AND (OL)

Reaction System (Tlc)		
1)=6)	Srp + c Brc	= a Opx + b Ol + d H_2O
2)=7)	Srp	= a Opx + b Ol + c Brc + d H_2O
3)=8)	Srp + b Ol	= a Opx + c Brc + d H_2O
4)=9)	Srp + b Ol + d H_2O	= a Opx + c Brc
5)=10)	b Ol + d H_2O	= Srp + a Opx + c Brc
Reaction System (Brc)		
1)=6)	Srp	= c Tlc + a Opx + b Ol + d H_2O
2)=7)	Srp + c Tlc	= a Opx + b Ol + d H_2O
3)=8)	Srp + a Opx	= c Tlc + b Ol + d H_2O
4)=9)	Srp + c Tlc + b Ol	= a Opx + d H_2O
5)=10)	Srp + a Opx + d H_2O	= c Tlc + b Ol
Reaction System (Opx)		
1)=5)	Srp	= a Ol + b Brc + c Tlc + d H_2O
2)=6)	Srp + b Brc	= a Ol + c Tlc + d H_2O
3)=7)	Srp + b Brc + c Tlc	= a Ol + d H_2O
4)=8)	+ b Brc + d H_2O	= Srp + a Ol + d H_2O
Reaction System (Ol)		
1)=5)	Srp	= b Brc + a Opx + c Tlc + d H_2O
2)=6)	Srp + b Brc	= a Opx + c Tlc + d H_2O
3)=7)	Srp + b Brc + c Tlc	= a Opx + d H_2O
4)=8)	+ b Brc + d H_2O	= Srp + a Opx + d H_2O

planes: {Brc} → {Ol} → {H_2O} → {Srp} → {Opx}, and reactions 6 → 10: sequence of zero planes: {Brc} → {Ol} → {H_2O} → {Srp}] explains the repetition of reaction configurations. The two groups of coinciding reactions are 1 to 5 and 6 to 10. Owing to reasons of symmetry across the rotation axis, reaction 1 coincides with 6, reaction 2 with 7, and so forth. Thus each reaction has its complementary counterpart, and only five *different* configurations are distinguished (Table 4).

If the Mg end-member in brucite is replaced by its Fe end-member, Figure 2b is obtained. Zero contours are still planes and obey the same rules as before. A zero plane of a specific mineral does not depend on its own composition. Compared to Figure 2a, all planes except {Fe-Brc} have moved. All zero contours now intersect the corner (0,0,0), but only {Fe-Brc} intersects (1,1,1) also. At this corner, "ferro-brucite" is the only phase containing Fe and is incompatible with the remaining phases. Its disappearance at (1,1,1) leaves the system univariant, and the reaction is

$$Srp = En + Fo + H_2O.$$

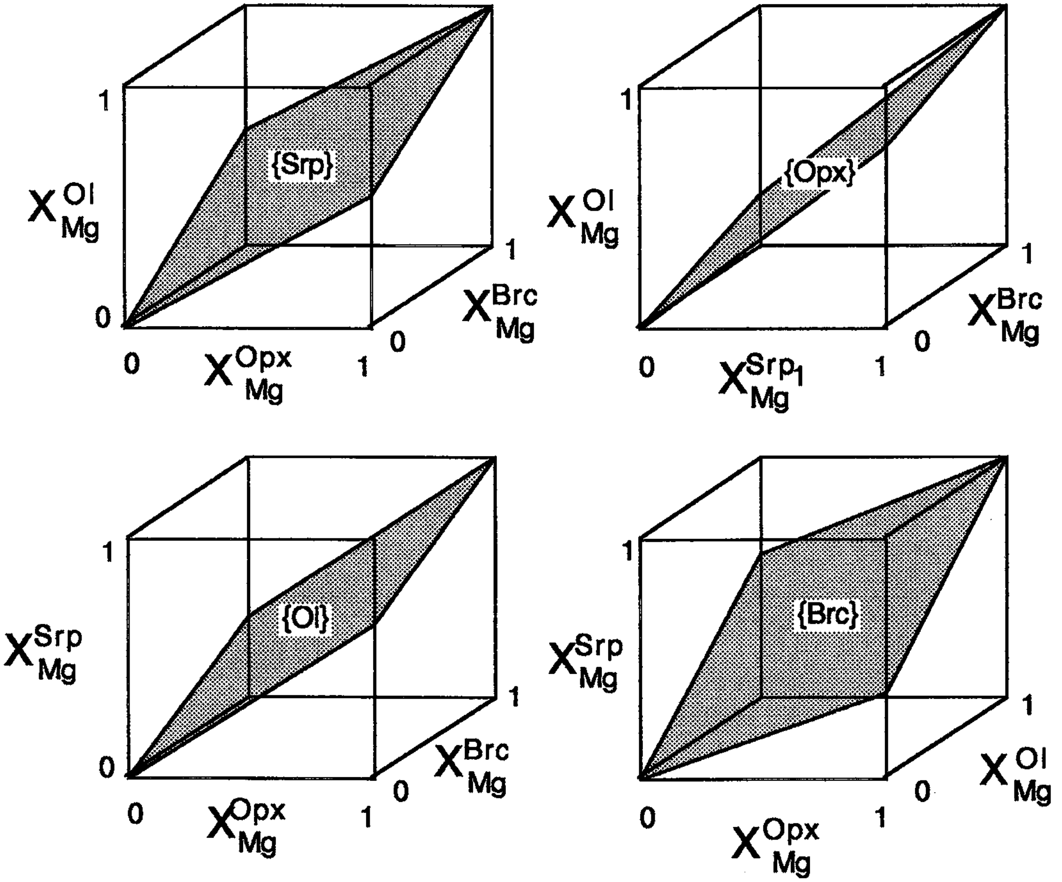

FIG. 3. Reaction subspaces for the system (Tlc). The zero plane of each mineral depends on the three mole fractions of coexisting minerals but not on their own composition. All the planes intersect (0,0,0) and (1,1,1) of their cubes.

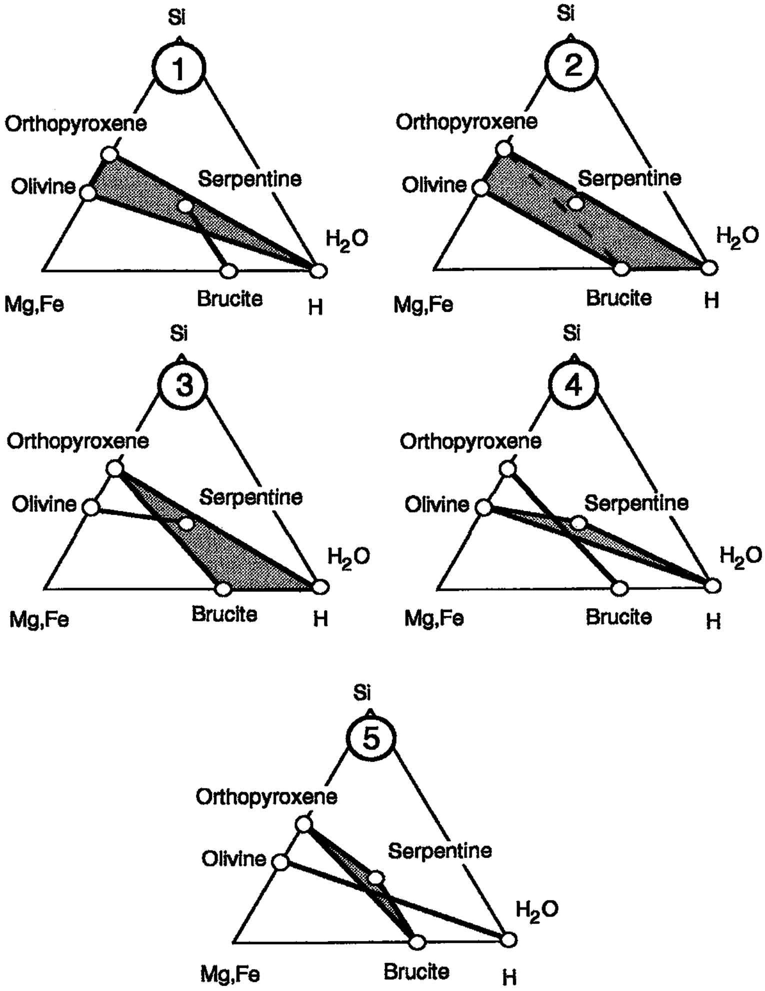

FIG. 4. The five valid configurations in the system (Tlc), derived by chemographic means. They correspond to those configurations obtained from Fig. 2, and are listed in Table 4.

This is the Mg-equivalent of the reaction at the Fe-corner in Figure 2a. Again, all the zero planes intersect in a common line, which is the rotation axis for the different zero planes. Again, ten different reaction-segments and five different configurations are distinguished (Table 4). Also shown by arrows in Figure 2b are the shifts of the zero planes due the change of brucite to its Fe-analog. All the zero planes, except {Brc}, underwent a parallel shift. If brucite is $Mg(OH)_2$, they all intersect (1,1,1); if brucite is $Fe(OH)_2$, they all intersect (0,0,0). Simultaneously, the rotation axis moves from the top part of the cube where it intersects $X_{Mg}^{Opx} = 0$, $X_{Mg}^{Ol} = 0.5$, $X_{Mg}^{Srp} = 0.33$ (Fig. 2a) to the bottom part, where it intersects $X_{Mg}^{Opx} = 1$, $X_{Mg}^{Ol} = 0.5$, $X_{Mg}^{Srp} = 0.66$ (Fig. 2b). The fact that {Brc} is the only stationary element in the two cubes, and that the rotation axis is always part of the zero plane of brucite, requires that the rotation axis moves along {Brc}.

Figure 2a can be transformed to Figure 2b by an inversion through the cube's center, $X_{Mg}^{Opx} = 0.5$, $X_{Mg}^{Ol} = 0.5$, $X_{Mg}^{Srp} = 0.5$. Also, the zero plane of brucite intersects this inversion point and itself is symmetrical. It is evident from Figures 2a and 2b *that the inversion point is also responsible for the inversion symmetry of reaction configurations in the cube.*

The fact that zero planes depend on three mole fractions (and not on all four) allows their display in reaction subspaces (Fig. 3). Each zero plane is shown in an individual subspace, which together form reaction hyperspace. The graphical display of reaction subspace does not allow the determination of reaction configurations. This problem can be solved by chemographic means. The chemography in Figure 1 allows for five different reaction-configurations (Fig. 4). These five configurations correspond to those listed in Table 4. Reaction configuration 1) is only possible if a major amount of serpentine reacts together with a minor amount of brucite to form olivine, orthopyroxene and H_2O: the more brucite, the less orthopyroxene. If brucite is absent (c = 0), equal molar amounts of orthopyroxene and olivine react to serpentine or *vice versa*. The reaction is

$$\mathrm{(Mg,Fe)_3Si_2O_5(OH)_4 = (Mg,Fe)_2SiO_4 + (Mg,Fe)SiO_3 + 2\ H_2O}$$

In reaction 2), serpentine is on the opposite side of all other phases present in the system. H_2O will always be on the same side as brucite, orthopyroxene and olivine because serpentine is outside the triangle olivine, orthopyroxene and brucite. In reaction 3), a large amount of serpentine and a small amount of olivine are on the opposite side of orthopyroxene, brucite and H_2O in the equation. H_2O may disappear if serpentine and olivine occur in a ratio that lies on the connecting line of orthopyroxene and brucite. The reaction then is

$$\mathrm{(Mg,Fe)_3Si_2O_5(OH)_4 + (Mg,Fe)_2SiO_4 = 3\ (Mg,Fe)SiO_3 + 2\ (Mg,Fe)(OH)_2}$$

In reaction 4), serpentine and olivine are joined by H_2O and balance for orthopyroxene and brucite. In equation 5), approximately equal molar amounts of olivine and H_2O react to orthopyroxene, brucite and serpentine.

Reaction system (Brc)

This reaction contains the four mole fractions $X^{\mathrm{Tlc}}_{\mathrm{Mg}}$, $X^{\mathrm{Opx}}_{\mathrm{Mg}}$, $X^{\mathrm{Ol}}_{\mathrm{Mg}}$ and $X^{\mathrm{Srp}}_{\mathrm{Mg}}$. The stoichiometric coefficient of H_2O, which is the only pure phase, depends on all four parameters, and its zero contour cannot be displayed graphically without simplifications. It is evident from

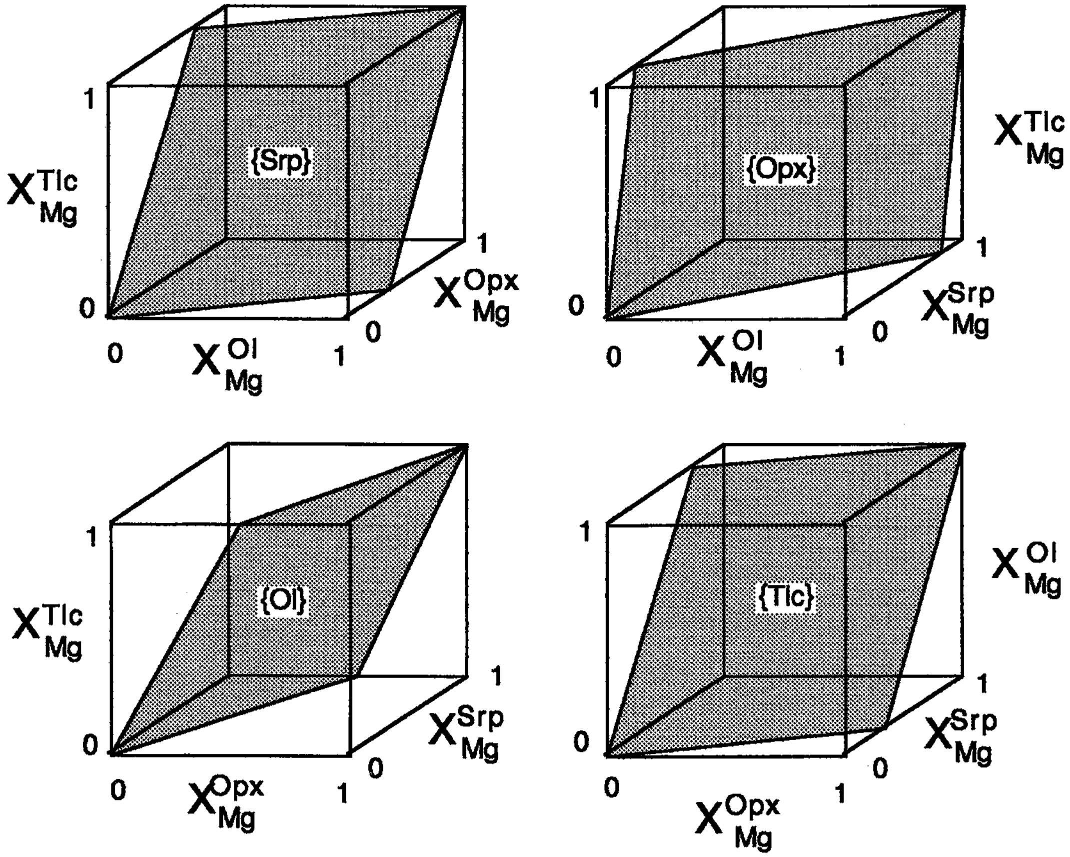

FIG. 5. Reaction subspaces for the system (Brc). The zero plane of each mineral depends on the three mole fractions of coexisting minerals but not on their own composition. All the planes intersect (0,0,0) and (1,1,1) of their cubes.

its stoichiometric coefficient (Table 3) that its zero contour has to intersect (0,0,0,0) as well as (1,1,1,1) of reaction hyperspace. The zero planes of the four solid-solution phases depend on three mole fractions only and not on the composition of these phases. The zero planes are displayed in the reaction subspaces of Figure 5. Each reaction cube is defined by a different set of mole fractions, and each of the four zero planes intersects the two corners (0,0,0) and (1,1,1) of the respective subspace (Fig. 5).

A zero plane that intersects the corner (0,0,0) of a reaction subspace and *does not depend on any other mole fraction* will also intersect the point (0,0,0,0) of hyperspace. The same applies to the two corners (1,1,1) and (1,1,1,1). This can be verified by inserting (0,0,0,0) and (1,1,1,1) into the different stoichiometric coefficients. As a result, not only does {H_2O} intersect the corners (0,0,0,0) and (1,1,1,1) of hyperspace, but so do {Srp}, {Opx}, {Ol} and {Tlc}. The two points (0,0,0,0) and (1,1,1,1) are connected by a line, which is the rotation axis around which all the zero contours rotate. It is the line where all stoichiometric coefficients become zero, and the reaction disappears.

Each of the zero contours cuts the hyperspace X_{Mg}^{Tlc}, X_{Mg}^{Opx}, X_{Mg}^{Ol}, X_{Mg}^{Srp} into two reaction segments. Five non-coinciding zero contours give rise to ten different reaction-segments and five different configurations. The evaluation of reaction configurations is possible by the use of chemographic rules. The different configurations are displayed in Figure 6 and listed in Table 4. Serpentine is the only phase that can react to the other four. It may coexist with either talc or orthopyroxene

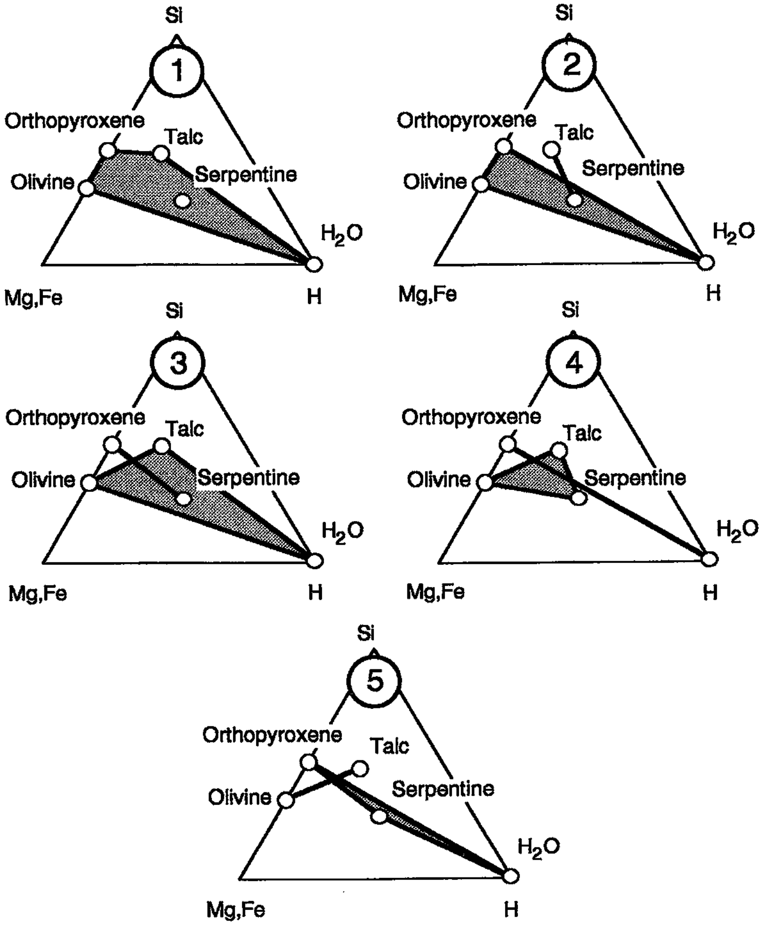

FIG. 6. The five valid reaction configurations in the system (Brc) and derived by chemographic means. The different configurations are listed in Table 4.

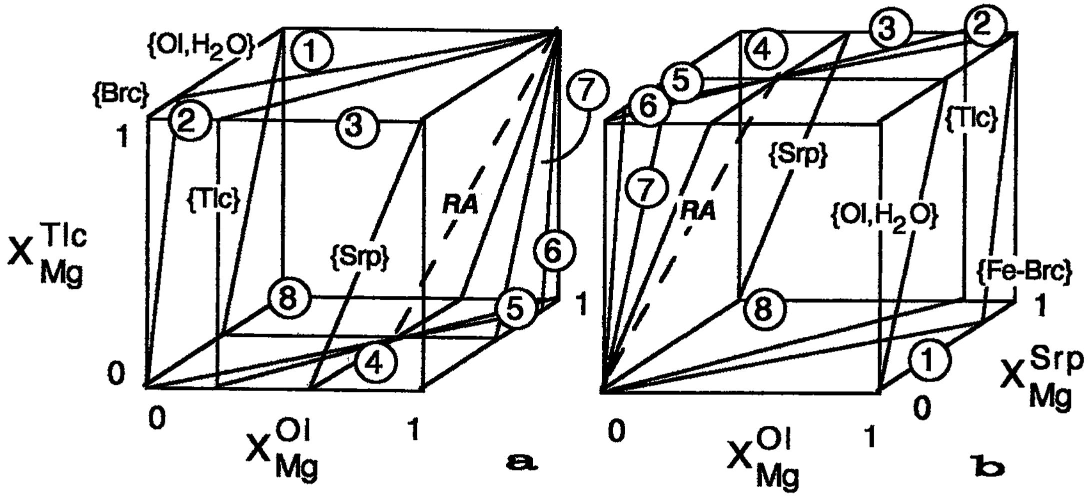

FIG. 7. Reaction subspaces for the system (Opx). Fig. 7a displays four zero planes with brucite as $Mg(OH)_2$; Fig. 7b shows four zero planes with brucite as $Fe(OH)_2$. The zero planes of Ol and H_2O coincide. Each cube can be derived from the other by a centrosymmetric inversion. The four valid reaction-configurations are listed in Table 4.

to react to the other three phases.

Reaction system (Opx)

Reaction subspaces are derived for either the Mg end-member (Fig. 7a, t = 1) or Fe end-member (Fig. 7b, t = 0) of brucite, respectively. Again the two reaction cubes are symmetrical and have a center of inversion at $X^{\rm Opx}_{\rm Mg} = 0.5$, $X^{\rm Ol}_{\rm Mg} = 0.5$, $X^{\rm Srp}_{\rm Mg} = 0.5$. This is also reflected in the symmetry of reaction configurations. Four different zero planes (the planes of olivine and H_2O coincide) allow for eight different reaction-segments. Olivine and H_2O are always on the same side of the equation.

If brucite is pure $Mg(OH)_2$, all the zero planes intersect the corner (1,1,1), as well as the point $X^{\rm Tlc}_{\rm Mg} = 0$, $X^{\rm Ol}_{\rm Mg} = 0.625$ and $X^{\rm Srp}_{\rm Mg} = 0.5$ of the reaction cube (Fig. 7a). The line connecting the two points is the rotation axis for the different zero planes and is the location where the reaction disappears. The corner (1,1,1) is intersected by all zero planes, whereas (0,0,0) is intersected by {Brc} only. The incompatibility of brucite with the Fe-corner (0,0,0) leaves the system univariant, and the equation is

$$1\ \text{Gre} = 1.2\ \text{Fa} + 0.1\ \text{Min} + 1.8\ H_2O.$$

With "ferro-brucite", all the zero contours intersect (0,0,0), and {Brc} also intersects (1,1,1). At (1,1,1) the reaction is

$$1\ \text{Ant} = 1.2\ \text{Fo} + 0.1\ \text{Tlc} + 1.8\ H_2O,$$

which is the Mg-analog of the reaction at (0,0,0). {Brc} in both figures coincides, and the rotation axis moves along this zero plane. It is also possible to derive the different reaction-configurations by chemographic means.

Reaction system (Ol)

This reaction system has similar features to the (Opx) reaction system. Two zero planes, (Opx) and (H_2O), coincide, and eight reaction segments or four different reaction-configurations are distinguished (Fig. 8, Table 4). Again, zero contours are planes and intersect along a rotation axis. This is true for both figures, if brucite is $Mg(OH)_2$ (Fig. 8a) or $Fe(OH)_2$ (Fig. 8b). The position of the rotation axis can be evaluated from the intersection of any two zero planes. If t = 0, the relationship between the different mole fractions is $u = 2z$ (Opx), and $u = 1.333v$ (Srp) using the zero planes of orthopyroxene and serpentine. If t = 1, the relationship is, for the same two planes, $u = 2z{-}1$ (Opx) and $u = 1.333v{-}1$ (Srp). The reaction at the Fe-corner, with brucite as incompatible phase, is

$$1\ \text{Gre} + 0.5\ \text{Min} = 6\ \text{Fs} + 3\ H_2O.$$

With "ferro-brucite" (t = 0), the reaction at (1,1,1) is

$$6\ \text{En} + 3\ H_2O = 1\ \text{Ant} + 0.5\ \text{Tlc}.$$

REACTION SYSTEMS INVOLVING TWO SERPENTINE MINERALS

Few data are available on the compositional relationship between coexisting serpentine minerals (Wicks & Plant 1979, Dungan 1979). The only cases of polymorph transformations known are from lizardite to chrysotile or from lizardite 1T to lizardite

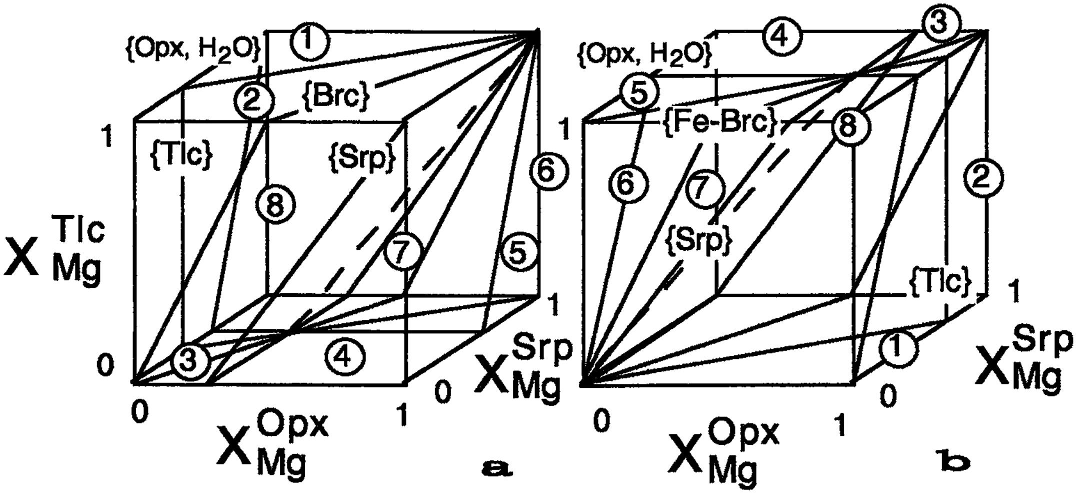

FIG. 8. Reaction subspaces for the system (Ol). Fig. 8a displays four zero planes with brucite as $Mg(OH)_2$; Fig. 8b shows four zero planes with brucite as $Fe(OH)_2$. The zero planes of orthopyroxene and H_2O coincide. Each cube can be derived from the other by a centrosymmetric inversion. The four valid reaction-configurations are listed in Table 4.

$2H_1$ (O'Hanley, written comm. 1992). In order to keep the discussion as general as possible, the two serpentine minerals will be distinguished as Srp_1 (*e.g.*, Ctl) with composition *x*, and Srp_2 (*e.g.*, Lz) with composition *y*. Five different "retrograde" reactions are discussed. The equations and the corresponding stoichiometric coefficients are listed in Table 5, the different configurations in Table 6.

TABLE 5 . REACTION SYSTEMS INCLUDING TWO SERPENTINE MINERALS

Reaction System (Tlc,Brc)

$$Srp_x + a\,Srp_y = b\,Opx_v + c\,Ol_w + d\,H_2O$$

$$a=\frac{v+2w-3x}{3y-v-2w},\; b=\frac{3(y-x)}{3y-v-2w},\; c=\frac{3(y-x)}{3y-v-2w},\; d=\frac{6(y-x)}{3y-v-2w}$$

Reaction System (Tlc,Opx)

$$Srp_x + a\,Srp_y = b\,Ol_w + c\,Brc_t + d\,H_2O$$

$$a=\frac{4w-3x-t}{3y-4w+t},\; b=\frac{6(y-x)}{3y-4w+t},\; c=\frac{3(x-y)}{3y-4w+t},\; d=\frac{9(y-x)}{3y-4w+t}$$

Reaction System (Tlc,Ol)

$$Srp_x + a\,Srp_y = b\,Opx_v + c\,Brc_t + d\,H_2O$$

$$a=\frac{3x-2v-t}{t+2v-3y},\; b=\frac{6(x-y)}{t+2v-3y},\; c=\frac{3(x-y)}{t+2v-3y},\; d=\frac{3(x-y)}{t+2v-3y}$$

Reaction System (Brc,Opx)

$$Srp_x + a\,Srp_y = b\,Ol_w + c\,Tlc_u + d\,H_2O$$

$$a=\frac{4w+u-5x}{5y-4w-u},\; b=\frac{6(y-x)}{5y-4w-u},\; c=\frac{(y-x)}{2(5y-4w-u)},\; d=\frac{9(y-x)}{5y-4w-u}$$

Reaction System (Brc,Ol)

$$Srp_x + a\,Srp_y = b\,Opx_v + c\,Tlc_u + d\,H_2O$$

$$a=\frac{2v-x-u}{u+y-2v},\; b=\frac{6(y-x)}{u+y-2v},\; c=\frac{x-y}{2(u+y-2v)},\; d=\frac{4(y-x)}{u+y-2v}$$

TABLE 6 . REACTION CONFIGURATIONS IN SYSTEMS INCLUDING TWO SERPENTINE MINERALS

Reaction System (Tlc,Opx)

1.)=4.) $Srp_1 + Srp_2 + Brc = Ol + H_2O$
2.)=5.) $Srp_1 + Brc = Srp_2 + Ol + H_2O$
3.)=6.) $Srp_1 + Ol + H_2O = Srp_2 + Brc$

Reaction System (Tlc,Ol)

1.)=4.) $Srp_1 + Srp_2 = Opx + Brc + H_2O$
2.)=5.) $Srp_1 = Srp_2 + Opx + Brc + H_2O$
3.)=6.) $Srp_1 + Opx + Brc + H_2O = Srp_2$

Reaction System (Brc,Opx)

1.)=4.) $Srp_1 + Srp_2 = Tlc + Ol + H_2O$
2.)=5.) $Srp_1 = Srp_2 + Tlc + Ol + H_2O$
3.)=6.) $Srp_1 + Tlc + Ol + H_2O = Srp_2$

Reaction System (Brc,Ol)

1.)=4.) $Srp_1 + Srp_2 + Tlc = + Opx + H_2O$
2.)=5.) $Srp_1 + Tlc = Srp_2 + Opx + H_2O$
3.)=6.) $Srp_1 + Opx + H_2O = Srp_2 + Tlc$

Reaction System (Tlc,Brc)

1.)=4.) $Srp_1 = Srp_2 + Opx + Ol + H_2O$
2.)=5.) $Srp_1 + Ol = Srp_2 + Opx + H_2O$
3.)=6.) $Srp_1 + Opx = Srp_2 + Ol + H_2O$

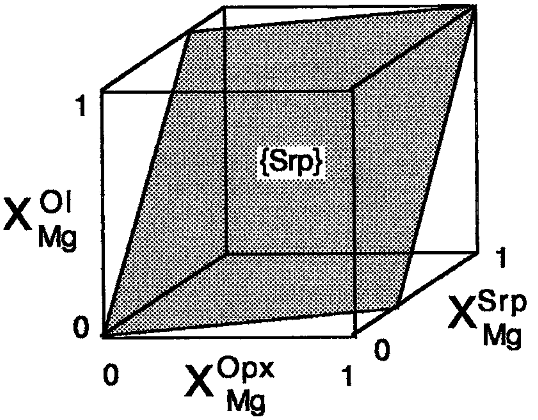

FIG. 9. Reaction cube for the system (Tlc,Brc). For all minerals except serpentine, the zero contour is a line at $x = y$, where the two serpentine minerals coincide in composition. The zero contour of both serpentine minerals are planes in a cube, with the mole fractions of olivine, orthopyroxene and the other serpentine as coordinate axes.

Reaction system (Tlc,Brc)

As will become evident below, reaction systems with two serpentine minerals have two types of zero contours. The one concerns the serpentines, the other concerns the remaining phases. The zero contour of the one serpentine mineral depends on the composition of the other serpentine mineral as well as that of the remaining solid-solutions. The zero planes of Srp_1 and Srp_2 coincide if the respective compositions are exchanged (Fig. 9). Zero contours other than for serpentine are lines in the reaction square $X^{Srp1}_{Mg} - X^{Srp2}_{Mg}$ and form the diagonal where the composition of the two serpentine minerals coincide ($x = y$). This line is equivalent to a polymorph transformation. On this line orthopyroxene, olivine and H_2O disappear, and the resulting equation is

$$Srp_1 = Srp_2.$$

At $x = y$, the system degenerates to one component, and two phases establish a univariant reaction. The fact that the two serpentine minerals have the same composition justifies the use of the term polymorph (Table 1). All the different zero contours intersect the points (0,0,0,0) and (1,1,1,1) of reaction hyperspace. Three independent zero contours allow for three different reaction-configurations, which are listed in Table 6. The fact that the zero contours of brucite, olivine and H_2O coincide has implications on possible reaction-configurations. The three minerals are always found on the same side of the equation. Only one possible configuration has to be found, and the others are evident.

Reaction systems (Tlc,Ol) and (Tlc,Opx)

The two systems show a number of similarities and are discussed together. Both contain four mole fractions, and reaction space is derived for either brucite or "ferro-brucite". Similar to the previous example, the zero contours of the two serpentine minerals depend on three mole fractions (Fig. 10), whereas the zero planes of the remaining phases are located where the two serpentine minerals coincide in composition. Three non-coinciding zero planes allow for three different configurations (Table 6). Brucite will always oppose olivine and H_2O in (Tlc,Opx) (Tables 5, 6). Olivine and H_2O may either join Srp_1 and are on the opposite side of Srp_2 and brucite, join Srp_2 and balance Srp_1 and brucite, or balance Srp_1, Srp_2 and brucite. In (Tlc,Ol) orthopyroxene, brucite and H_2O are always on the same side of the equation (Tables 5, 6), and they may either coexist with Srp_1 or Srp_2 or balance them. This example shows that the number of possible reaction-configurations is quite limited, and that some configurations, like orthopyroxene and brucite on opposite sides in the equation, are *chemically* not possible. In both reaction systems, the three independent zero planes intersect in a common line, around which the zero planes rotate and the reaction disappears. The rotation axis is part of the "plane of polymorphic transformation". If brucite is $Mg(OH)_2$ ($t = 1$), the different zero planes intersect the Mg-corner (1,1,1), where no reaction is possible but only the plane of polymorphic transformation also intersects (0,0,0). The rotation axis cuts through (1,1,1), but not through (0,0,0). The reaction at the Fe-corner (0,0,0) is

$$Gre_1 = Gre_2$$

where the two greenalite minerals have different structures. Whether such a polymorphic transition, similar to that in the serpentine system, is possible is not known and hypothetical.

With "ferro-brucite" ($t = 0$), all zero planes intersect the Fe-corner (0,0,0) where no reaction is possible. But only the plane of polymorph transformation also intersects (1,1,1). The rotation axis now intersects (0,0,0) but not (1,1,1). The reaction at the Mg-corner is

$$Srp_1 = Srp_2.$$

The two systems in Figures 10a and 10b are related by centers of inversion. The system with "ferro-brucite" can be obtained from the one with brucite through a centrosymmetric inversion.

The corners (0,0,0) and (1,1,1) only host a reaction if brucite is assigned a fixed end-member composition. If this restriction is not imposed, no reaction is possible at the two corners.

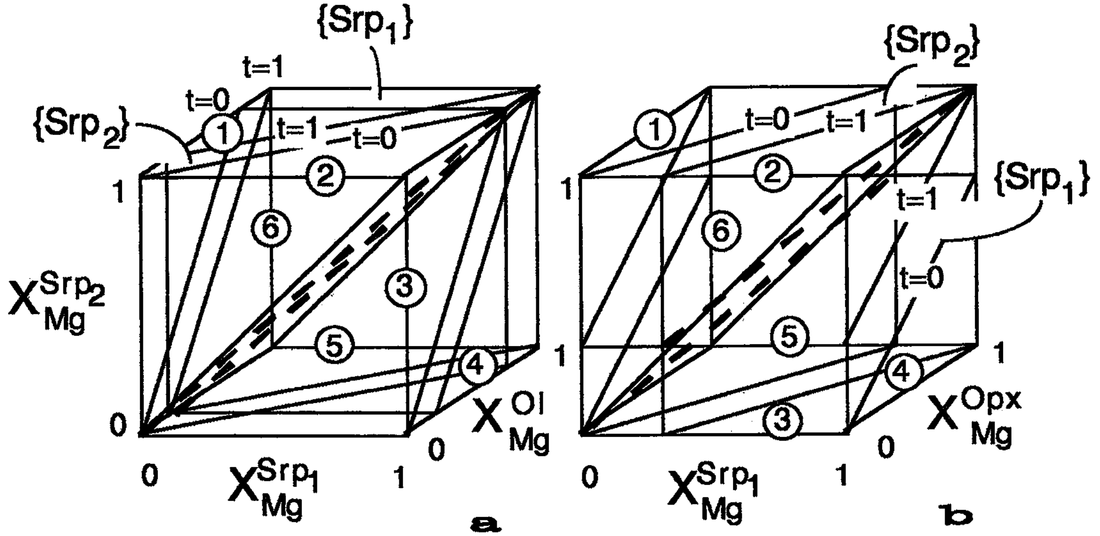

FIG. 10. Reaction subspaces for the systems (Tlc,Ol) and (Tlc,Opx). Fig. 10a displays three zero planes for (Tlc,Opx) with brucite as either $Mg(OH)_2$ (t = 1) or as $Fe(OH)_2$ (t = 0). Fig. 10b shows the equivalent for (Tlc,Ol). The zero planes of all minerals except the serpentines coincide at $x = y$. Three zero planes allow for three different reaction-configurations (Table 6). The dashed lines in each of the two figures represent the rotation axes for either t = 0 or 1, where all the zero planes intersect and no reaction is possible.

Reaction systems (Brc,Opx) and (Brc,Ol)

The two systems show a number of similarities. Both contain four mole fractions giving rise to reaction hyperspace. The two serpentine minerals describe two different zero planes, whereas the remaining solid phases change their signs at the line of polymorphic transformation ($x = y$). All zero contours intersect both corners, (0,0,0,0) and (1,1,1,1), of reaction hyperspace $u - v/w - x - y$ ($X^{Tlc}_{Mg} - X^{Opx}_{Mg}/X^{Ol}_{Mg} - X^{Srp1}_{Mg} - X^{Srp2}_{Mg}$). Both corners are overdetermined and unable to provide a specific reaction-equation. Three non-coinciding zero contours allow for three different reaction-configurations. These are listed in Table 6.

APPLICATION TO AN OPEN SYSTEM

Closed systems are limiting cases of open ones where the exchange of ions with external sources and sinks is zero. Techniques of continuous reactions are not restricted to closed systems (Thompson 1982a, b). The following case, concerned with serpentinization in layered rocks of the Bushveld complex, includes the transfer of species through an aqueous phase.

Textures and mineral compositions

The rocks described below are part of the Upper Critical Zone of the Bushveld Complex (see SACS 1980, for nomenclature and lithology); serpentinization is typically observed adjacent to pegmatites, concordant to the layering. A detailed description of both the layered rocks and the pegmatites is given by Van Zyl (1970).

The wallrocks of concordant pegmatites show a variable intensity of alteration. Fresh rock consists of six- to eight-sided euhedral prisms of orthopyroxene, poikilitically enclosed in plagioclase. Alteration is visible both macroscopically as well as microscopically. In a hand specimen, plagioclase changes its color from gray transparent to white translucent. In the microscope, the feldspar is seen to have altered to sericite (Van Zyl 1970), and serpentine and olivine appear. Olivine grains are either six- to eight-sided or have a round shape, and may be accompanied by parallel plates of biotite (Fig. 11b).

Parallel plates of biotite in the Upper Critical Zone typically occur adjacent to corroded grains of orthopyroxene and are a common texture in layered norite (Fig. 11a; Zingg, in prep.). Adjacent to orthopyroxene, (001) of mica parallels (100) of orthopyroxene. On the basis of petrographic observations, different stages in the formation of the parallel plates are observed in the norite. In a first stage, hornblende lamellae form crystallographically oriented replacement-induced features (McCallum, pers. comm.) along (100) of the original orthopyroxene. In a second stage, the pyroxene rims are overgrown by plagioclase, and the hornblende lamellae transform to biotite while enclosed in the newly formed feldspar. This second stage is the one

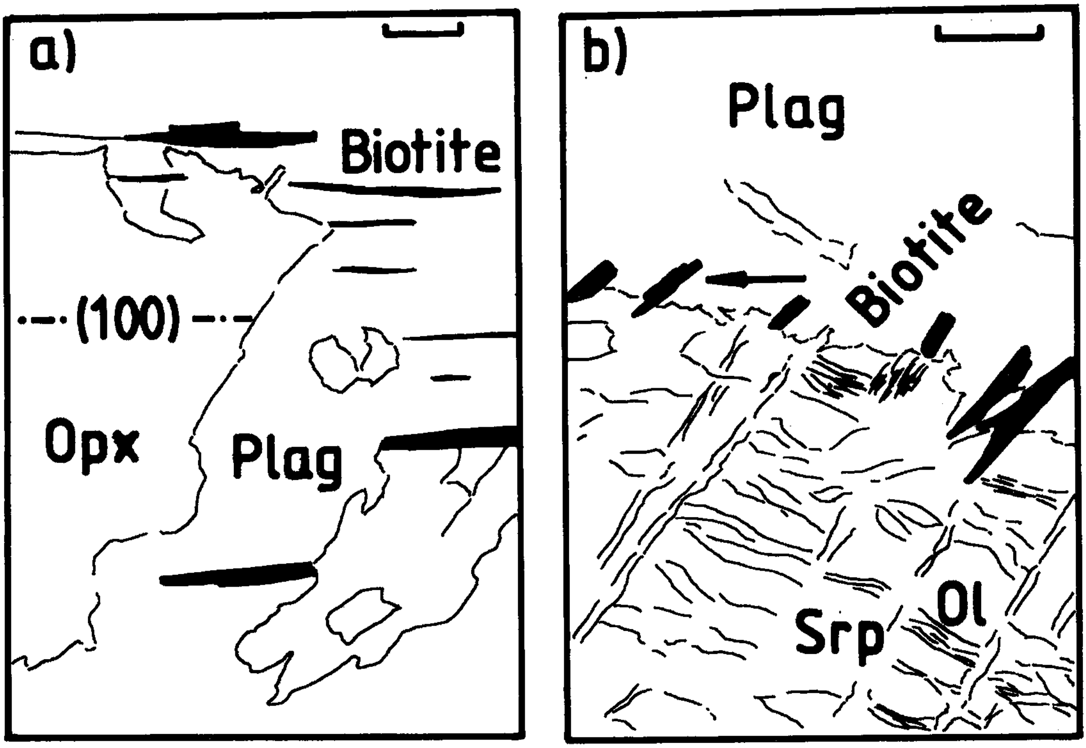

FIG. 11. a. Parallel plates of biotite adjacent to orthopyroxene in layered norite. The (001) plane of the plates parallels (100) of the orthopyroxene. The orthopyroxene is corroded and overgrown by plagioclase. The biotite plates transformed from hornblende lamellae while the orthopyroxene was replaced by plagioclase (plane-polarized light, scale bar = 0.1 mm). b. Parallel plates of biotite adjacent to olivine coexisting with serpentine. The orientation of olivine is at random to the orientation of the mica plates (crossed nicols, scale bar = 0.1 mm).

normally observed (Fig. 11a).

In the pyroxenite, adjacent to the concordant bodies of pegmatite, only one stage is observed. These are the parallel plates of biotite adjacent to olivine–serpentine textures. These biotite plates attest to the original presence of the orthopyroxene. Adjacent to olivine, the plates are still in parallel orientation (not parallel to the layering) and do not correlate with any optical orientation of the olivine. The observations are interpreted to indicate that hornblende, originally enclosed in orthopyroxene, transformed to biotite, whereas pyroxene was replaced by olivine. If grains of olivine have a six- to eight-sided shape, the olivine is a pseudomorph after orthopyroxene (type I). If grains of olivine are round, they seem to overgrow the original orthopyroxene, and the replacement is probably coupled with an increase in volume. In some cases, a fresh new rim of orthopyroxene (type II) may be seen to accumulate around the olivine.

Mineral compositions from samples adjacent to the concordant bodies of pegmatite are as follows:

TABLE 7. SERPENTINIZATION IN BUSHVELD LAYERED ROCKS

The Reaction

$$\mathrm{Mg_zFe_{1-z})_3Si_2O_5(OH)_4 = a\ Mg_vFe_{1-v}SiO_3 + b\ (Mg_wFe_{1-w})_2SiO_4 + c\ Si^{4+}}$$

$$\mathrm{+\ d\ Mg^{2+} + e\ Fe^{2+}}$$

Stoichiometric Coefficients

$$a = \frac{3(w-z)+d(1-w)-ew}{w-v}\ ,\ b = \frac{3(z-v)+d(v-1)+ev}{2(w-v)}$$

$$c = \frac{3z-2w-v+d(2w-v-1)+e(2w-v)}{2(w-v)}$$

Reaction Configurations

1.)	Srp				=		a Opx	+ b Ol	+ c Si^{4+}
2.)	Srp		+ Si^{4+}		=		a Opx	+ b Ol	
3.)	Srp +	b Ol	+ Si^{4+}		=		a Opx		
4.)		b Ol	+ Si^{4+}		=	Srp +	a Opx		
5.)		b Ol	+ Si^{4+}		=	Srp			
6.)		b Ol			=	Srp			+ c Si^{4+}
7.)				a Opx	=	Srp		+ b Ol	+ c Si^{4+}
8.)	Srp +			a Opx	=			b Ol	+ c Si^{4+}

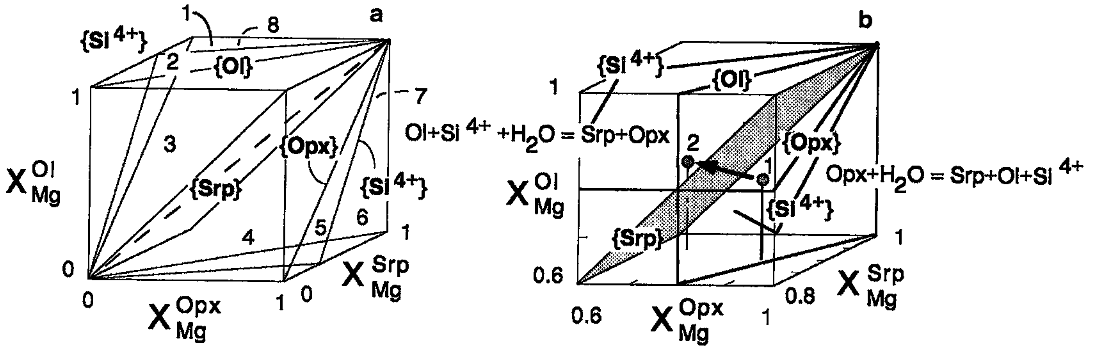

FIG. 12. a. Reaction space for the reaction $Srp_z = Opx_v + Ol_w + Si^{4+} + H_2O$ (Table 7). Four noncoinciding zero planes and four different reaction-configurations are distinguished. b. Mineral compositions plotted into the cube suggest two coupled reactions: 1) $Opx + H_2O = Srp + Ol + Si^{4+}$ (segment 7), and 2) $Ol + H_2O + Si^{4+} = Srp + Opx$ (segment 8).

$Mg/(Mg+Fe)_{Srp} = 0.90$ (± 0.01), $Mg/(Mg+Fe)_{Ol} = 0.79$ (± 0.05), $Mg/(Mg+Fe)_{Opx\ I} = 0.85$, $Mg/(Mg+Fe)_{Opx\ II} = 0.75$ (± 0.05).

The textures can be interpreted in two ways; either orthopyroxene (+ hornblende) transformed to olivine (+ biotite) and serpentine in one stage, or orthopyroxene first transformed to olivine and, in a second stage, olivine to serpentine. In the following, both cases will be considered. The two-pyroxene geothermometer (Lindsley 1983) suggests a temperature of re-equilibration of around 550° (± 50°) C.

Reaction relationship

Model 1: Opx → Ol + Srp and Ol → Srp + Opx

Only the major mineral phases are taken into account. These are serpentine, orthopyroxene and olivine. Magnetite, biotite, hornblende and talc are present in minor (< 2 vol.%) to trace amounts and will be disregarded. The system investigated consists of the four components, $MgO–FeO–SiO_2–H_2O$, and allows the determination of four stoichiometric coefficients (including H_2O). If the equation is normalized to one mole of serpentine and H_2O, three components (excluding H_2O) allow the determination of the stoichiometries of orthopyroxene, olivine and of one cation. The reaction, on which model 1 is based, is as follows:

$$Srp_z + i\,H^+ = a\,Opx_v + b\,Ol_w + c\,Si^{4+} + d\,Mg^{2+} + e\,Fe^{2+} + j\,H_2O.$$

The full equation and the stoichiometric coefficients are listed in Table 7, and the reaction cube is shown in Figure 12a. Four zero planes, eight reaction-segments (Table 7) and four different configurations are distinguished. Mineral compositions are plotted in Figure 12b and suggest the following two equations.

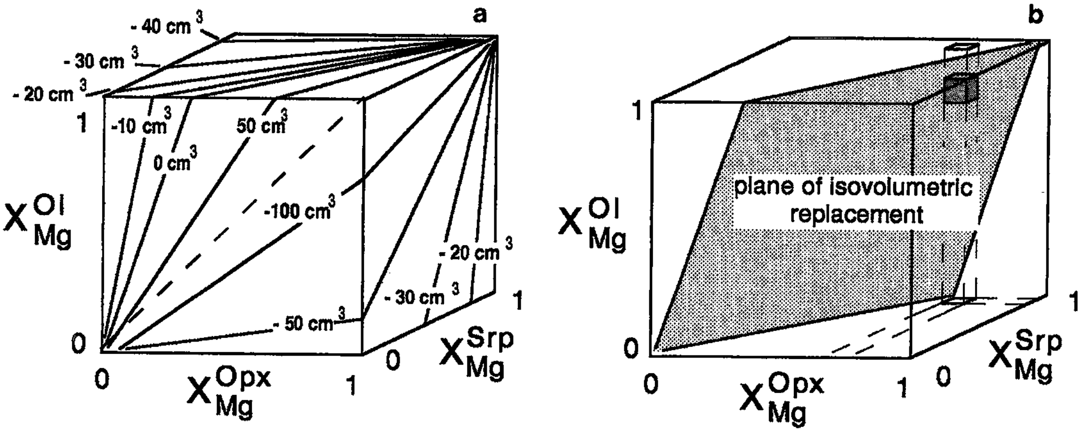

FIG. 13. a. Planes of constant volume of reaction recorded in the reaction cube X^{Ol}_{Mg}, X^{Opx}_{Mg} and X^{Srp}_{Mg}. b. Mineral compositions form the Critical Zone plot close to the plane of isovolumetric transformation.

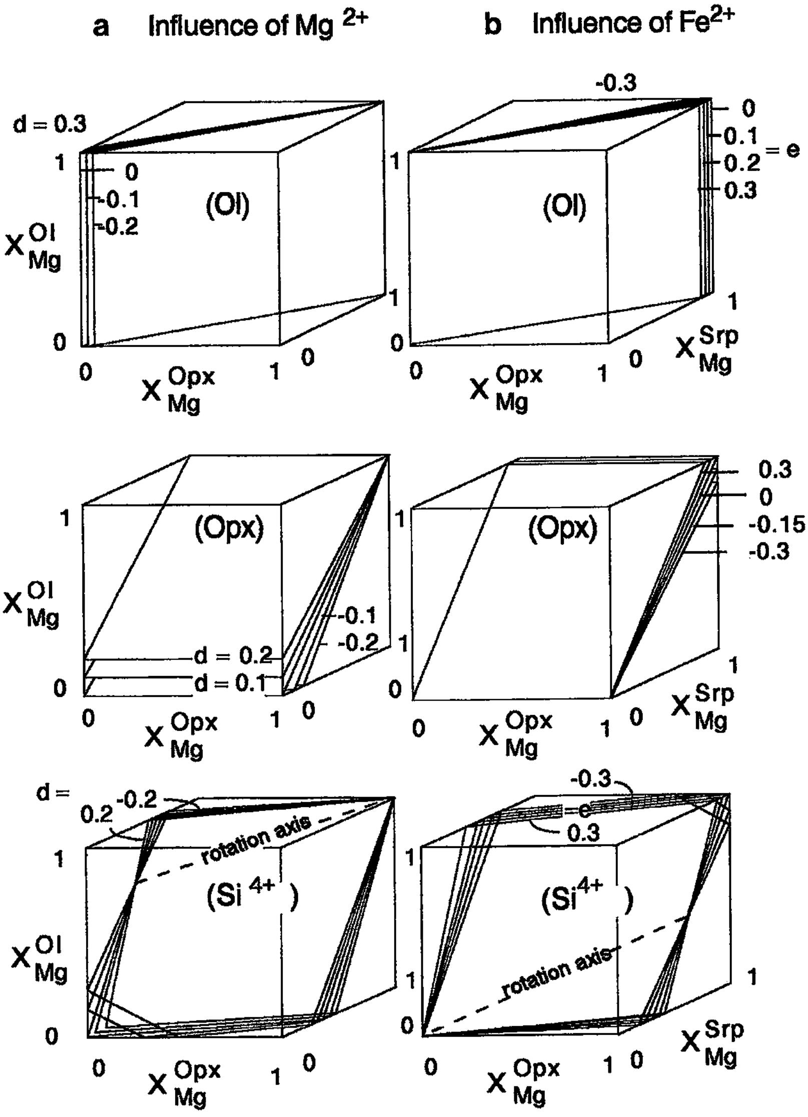

FIG. 14. a. Influence of Mg^{2+} on the zero planes of olivine, orthopyroxene and Si^{4+}. The Mg-corner is virtually unaffected by transfer of Mg^{2+}. b. Influence of Fe^{2+} on the zero planes of olivine, orthopyroxene and Si^{4+}. The largest influence of Fe^{2+} is experienced at the Mg-corner of the reaction cube.

The reaction including the corroded orthopyroxene relic plots in reaction-segment 7 (Fig. 12b)

$$a\ Opx_v + H_2O \rightarrow Srp_z + b\ Ol_w + c\ Si^{4+}.$$

The composition of the fresh orthopyroxene in the rim plots in segment 8 (Fig. 12b)

$$b\ Ol + c\ Si^{4+} + H_2O \rightarrow Srp + a\ Opx.$$

In both reactions, the driving force was an increase in $\mu(H_2O)$. In the first equation, Si^{4+} is removed, and orthopyroxene transforms to olivine. Simultaneously,

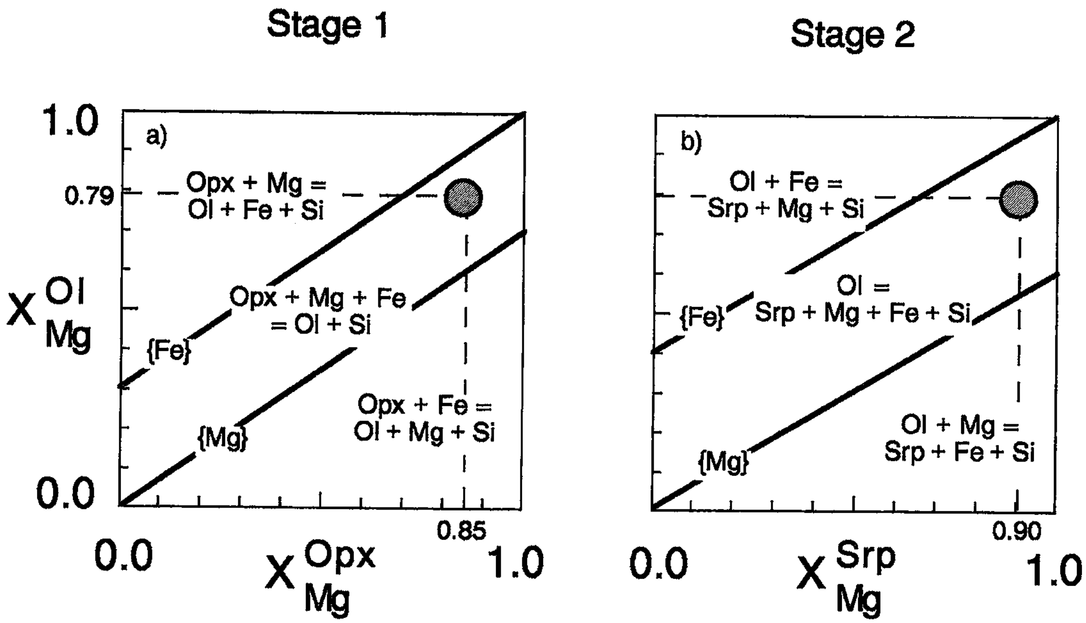

FIG. 15. a. Reaction square for the reaction Opx + Mg^{2+} + Fe^{2+} = Ol + Si^{4+}. The zero lines of Fe^{2+} and Mg^{2+} subdivide the square into three different reaction-segments. The dot records the composition of olivine and orthopyroxene. The model is based on a pseudomorphic replacement. b. Reaction square for the reaction Ol + Fe^{2+} + Mg^{2+} = Srp + Si^{4+}. Again, the zero lines of Fe^{2+} and Mg^{2+} subdivide the square into three different reaction-segments. The dot records the composition of olivine + serpentine. This model also is based on a pseudomorphic replacement.

an increase in $\mu(H_2O)$ causes serpentine to form. At a later stage, the fluid phase became enriched in silica, causing olivine to react back to orthopyroxene. Serpentine was still being produced. The volume of reaction of solids ΔV_s was calculated on the basis of molar data by Helgeson *et al.* (1978). Planes of constant ΔV_s are shown in Figure 13a. Mineral compositions plot near the plane of isovolumetric replacement (Fig. 13b). The influence of Mg^{2+} and Fe^{2+} on the zero planes of olivine, orthopyroxene and Si^{4+} is shown in Figure 14. The transfer of Mg^{2+} has little effect on the zero planes in the Mg-rich corners of reaction space. Only substantial supply of Fe^{2+} could alter the conclusions reached. In such a case, however, the silicates should be Fe-enriched, a feature not observed.

Model 2: Opx → Ol → Srp

This model takes advantage of the fact that the transformation takes place within the original grain-boundary of orthopyroxene. The olivine-serpentine texture does occupy the six- to eight-sided shape that define the original grains of orthopyroxene. In a first stage, orthopyroxene transforms to olivine,

$$(Mg_xFe_{1-x})SiO_3 + a\,Mg^{2+} + b\,Fe^{2+} + i/2\,H_2O = 0.71\,(Mg_yFe_{1-y})_2SiO_4 + c\,Si^{4+} + i\,H^+.$$

The stoichiometric coefficient of olivine is provided by the volume restriction (for solid phases only), and the remaining coefficients are: $a = 1.42\,y - x$, $b = 0.42 + x - 1.42\,y$, $c = 0.29$, $i = 2\,(a+b) - 4c$.

The zero contours for a and b are composition-dependent and are shown, together with compositional data, in Figure 15 (Stage 1). Mineral compositions suggest the equation

$$(Mg_{0.85}Fe_{0.15})SiO_3 + 0.27\,Mg^{2+} + 0.15\,Fe^{2+} + 0.32\,H^+ = 0.71\,(Mg_{0.79}Fe_{0.21})_2SiO_4 + 0.29\,Si^{4+} + 0.16\,H_2O.$$

Mg^{2+} and Fe^{2+} are supplied, and Si^{4+} is removed.

In the second stage, olivine is transformed to serpentine without altering the pseudomorphic texture.

$$(Mg_yFe_{1-y})_2SiO_4 + a\,Si^{4+} + (i/2 - 0.8)\,H_2O = 0.40\,(Mg_zFe_{1-z})_3Si_2O_5(OH_4) + b\,Fe^{2+} + c\,Mg^{2+} + i\,H^+.$$

The coefficient of serpentine was again obtained from the volume restriction. As long as the two minerals have roughly similar Mg/(Mg+Fe) ratios, the error introduced by neglecting the compositional dependency on the volume is minor. The zero contours for Fe^{2+} and Mg^{2+} are shown in Figure 15 (Stage 2), and mineral compositions suggest the reaction

$$(Mg_{0.79}Fe_{0.21})_2SiO_4 + 2.4\ H^+ =$$
$$0.40\ (Mg_zFe_{1-z})_3Si_2O_5(OH_4) + 0.2\ Si^{4+} +$$
$$0.3\ Fe^{2+} + 0.5\ Mg^{2+} + 0.4\ H_2O.$$

The transformation of olivine to serpentine is accompanied by the release of all cations involved. Also, this model can explain the appearance of a fresh rim of orthopyroxene around pseudomorphic textures. Both models are able to explain the textures observed.

SUMMARY AND CONCLUSIONS

In the ternary system $MgO–SiO_2–H_2O$, three solid phases are required to describe a univariant reaction. These could be one serpentine mineral, olivine and brucite. Normally, more than three phases are observed in serpentinized rocks (Thayer 1966, Coleman & Keith 1971, Dietrich & Peters 1971, Frost 1975, Wicks & Plant 1979, Laurent & Hébert 1979). Among the additional phases could be a second serpentine mineral, talc or orthopyroxene, among others. To be univariant, the system $FeO–MgO–SiO_2–H_2O$ requires four mineral phases. The treatment of FeO and MgO as independent components is reasonable only if solid solutions are taken into account.

Nine different reaction-systems have been derived, four including one and five including two serpentine minerals. The nine systems and the respective reaction-spaces contain an infinite number of single reactions, where an infinitesimal change in composition leads to an infinitesimal change in the stoichiometries of reactant and product phases. All the different reactions are grouped into different configurations. Each configuration occupies one volume segment in reaction space and is delimited by other zero contours.

Zero contours in systems with the exchange vector $FeMg_{-1}$ show some characteristic features. The zero contour of a solid-solution phase depends on the composition of other solution phases and is independent of its own composition. Zero contours of pure phases (*e.g.*, H_2O) in turn depend on all the mole fractions of the system. Zero contours are simple lines or planes. In the absence of pure phases, all zero contours intersect (0,0,0,(0)) and (1,1,1,(1)) of reaction (hyper)space. At these corners, the system loses one of its components, whereas the number of phases remains constant. The system is overdetermined. In the presence of a pure Mg-phase, its zero contour will intersect the Fe-corner (0,0,0,(0)), with which it is incompatible. The remaining solid-solution phases, however, will not intersect the Fe-corner, and a univariant reaction results. The same applies for a pure Fe-phase at the Mg-corner (1,1,1,(1)).

All zero contours in Fe–Mg systems intersect in a common line. The line is the rotation axis for the different zero planes. Two zero planes will always intersect in a line, where the two minerals disappear simultaneously. The disappearance of two minerals causes the degeneration of the system; the remaining phases have to disappear as well. In the absence of pure mineral phases, rotation takes place along the body diagonal through reaction (hyper)space, connecting (0,0,0,....) and (1,1,1,...). The rotation axis is the location where the ratio Mg:Fe coincides for all the solid solutions. The system degenerates to a simpler one, with three instead of four components. The components are $Mg_xFe_{1-x}O – SiO_2 – H_2O$. In the presence of a pure phase, the rotation axis will move away from that corner with which the pure phase is incompatible. The corner is characterized by a univariant reaction. Rotation axes are intrinsic features of systems including the $FeMg_{-1}$ exchange vector. Each zero contour subdivides reaction space into two segments. In a path around the rotation axis, each zero contour is crossed twice. After a 360° rotation, the original equation is reached again. This is possible only if each phase changes its side in the equation twice. Each reaction configuration is met twice in a round trip of 360° around the rotation axis. The number of reaction segments is thus twice that of reaction configurations in systems including the $FeMg_{-1}$ exchange vector.

In systems with two serpentine polymorphs, the line of polymorph transformation is another degeneracy. All components combine to one, which coincides with the composition of the two polymorphs. Two phases are required to form a univariant reaction in a unary system. In a study on serpentinization including two serpentine polymorphs, it is therefore of vital importance to know the compositions of both polymorphs. Does the presence of two polymorphs imply an intracrystalline transformation or are other minerals involved as well? The zero contours of the two serpentine minerals are related. The one for srp_1 depends on the composition of srp_2 and of the remaining solid-solution phases, the one for srp_2 depends on the composition of srp_1 and the remaining phases. If the mole fractions of srp_1 is exchanged with that of srp_2, the zero contour of the two serpentine minerals coincide.

In a first study introducing the present technique (Zingg 1991), reaction space was either a line, a square or a cube. Zero contours were points, lines or surfaces. Reaction space is graphically explorable as long as the number of solid solutions does not exceed three. With the exchange vector $FeMg_{-1}$, which is ubiquitous in most rock systems, even in the simple quaternary system presented in this study, reaction space has more than three dimensions, and constitutes a hyperspace. The rules governing reaction hyperspace are analogous to the rules of reaction space of lower dimension.

Reaction hyperspace can always be reduced to three dimensions by assigning fixed compositions to specific minerals of solid solution. In hyperspace, the evaluation of all possible reaction configurations is possible using the combination of a) chemography, and b) the rule: number of zero contours = number of configuration. If reaction cubes are constructed by keeping one of the mole fractions fixed at 0 or 1, the two cubes are related. The first can be derived from the second *via* a centrosymmetric inversion in reaction space. This inversion point is also responsible for symmetrically arranged reaction-configurations.

Reactions provide quantitative answers on a number of questions. The technique can be expanded to phase-equilibria studies, volume of reaction and mass-transfer calculations, among others. The technique seems suitable for extension to other multisystems like $CaO - MgO - FeO - SiO_2 - H_2O$, $MgO - FeO - Al_2O_3 - SiO_2 - H_2O$ and $MgO - FeO - Fe_2O_3 - SiO_2 - H_2O$.

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