Phase composition as a measure of reaction progress and an experimental model for the high-temperature metamorphism of mafic igneous rocks

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Abstract

A general method is presented by which the composition of phases in metamorphosed mafic igneous rocks can be used to quantitatively measure the progress of mineral–fluid reactions which proceed during metamorphism. The method is applied to the experimental hydrothermal phase equilibrium study of a mid-ocean ridge tholeiite by Spear (1981), and metamorphism of mafic rock by a variety of processes is modelled at temperatures between 600° and 900°C: (a) isobaric contact metamorphism at buffered oxygen fugacity; (b) isothermal metamorphism with increasing pressure at buffered oxygen fugacity; (c) metamorphism along a "normal" and a "low" geothermal gradient at buffered oxygen fugacity; (d) isothermal, isobaric oxidation; and (e) isobaric oxidation with increasing temperature. The model metamorphic events are characterized in terms of (1) overall prograde mineral–fluid reactions; (2) rock modes; (3) changes in rock volume; (4) identity and amounts of volatile species evolved and consumed; (5) amount of $P-V$ work performed by rock on its surroundings or vice versa; (6) amount of heat absorbed or released by rock; and (7) the interaction of rock with external fluid reservoirs during progress of the reactions. Two results are unexpected. First, metamorphism with increasing temperature at oxygen fugacity controlled by the quartz–fayalite–magnetite (QFM) buffer involves reduction of rock as mineral–fluid reactions consume H_2 and release H_2O. In contrast, the concentration of H_2 in fluid during metamorphism under redox conditions controlled by the hematite–magnetite (HM) buffer is sufficiently small that rock is neither reduced nor oxidized with increasing temperature. Second, model calculations indicate that at least 14–23 rock volumes of H_2O fluid are required to oxidize mafic rock from conditions of the QFM buffer to conditions of the HM buffer. The measured progress of dehydration/oxidation reactions that occur, for example, during contact metamorphism involving hydrothermal circulation of heated, oxidizing, meteoric water, therefore, may serve as a very sensitive monitor of the amount and pattern of fluid transport in the earth's crust.

Introduction

Metamorphosed mafic igneous rocks—blueschists, greenschists, amphibolites, and mafic granulites—constitute a significant portion of many metamorphic terranes. Changes in the mineralogy of these rocks have long been used as monitors of the grade of progressive metamorphism. In the last fifteen years a number of laboratory phase equilibrium studies have established the relationship between the phase assemblage of metamorphosed mafic igneous rocks and the pressure, temperature, and oxygen fugacity which prevailed during their formation (Binns, 1968; Liou et al., 1974; Spear, 1981; Moody et al., 1983). Both the experimental studies and recent work on natural metamorphic rocks (e.g., Harte and Graham, 1975; Laird, 1980; Laird and Albee, 1981a,b) demonstrate that prograde mineral reactions in mafic rocks are largely of the continuous variety (cf. Thompson et al., 1982). Although the mineral assemblage in these rocks does change over large ranges in temperature or grade, there are significant intervals in temperature or grade in which mafic rocks contain the same assemblage of minerals; the minerals react with each other, thereby changing mineral compositions and proportions, but neither do new minerals appear nor do old minerals disappear.

The mineralogical evolution of mafic igneous rocks during metamorphism has recently been systematized by Thompson et al. (1982). They factored the overall prograde mineral reaction into a set of component reactions and presented a method by which the progress of the component reactions (and hence the overall reaction) could be measured either by modal analysis of rocks or by

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the composition of constituent mineral phases (or both). Thompson et al. examined with their strategy mineral reactions both in natural mafic schists and in the phase equilibrium experiments of Liou et al. (1974). This paper builds upon the pioneering study of Thompson et al. (1982) by developing a model for the metamorphism of mafic igneous rocks from the experimental study of Spear (1981). In the first part of the paper, a method is presented by which the compositions of coexisting mineral phases in mafic rocks can serve as quantitative monitors of reaction progress. Spear's results are used to measure reaction progress as a function of changes in pressure, temperature, and oxygen fugacity, and to determine the mineralogy of mafic rock under a variety of high-temperature conditions (600–900°C) appropriate both to contact and regional metamorphism. Calculated results not only model the appearance of new minerals and disappearance of old minerals in mafic rocks, but also identify the continuous reactions that occur over much of the metamorphic history of this rock type. Next a number of metamorphic processes or environments are identified: (a) isobaric metamorphism caused by increasing temperature; (b) isothermal metamorphism caused by increasing pressure; (c) metamorphism along a "low" geothermal gradient; (d) metamorphism along a "normal" geothermal gradient; (e) isobaric, isothermal metamorphism caused by oxidation; and (f) isobaric metamorphism caused by oxidation and increasing temperature. Using the measured values of reaction progress, metamorphism in each of the six environments is characterized in terms of the following: (1) the overall prograde mineral reactions; (2) rock modes; (3) changes in rock volume; (4) the identity and quantity of volatile species released or consumed; (5) P–V work performed by rock on its environment or vice versa; (6) interaction of rock with external heat reservoirs; and (7) interaction of rock with external fluid reservoirs. Results integrate a variety of phenomena that occur during metamorphism and show their temporal interrelationships.

Phases, components, phase composition, and net-transfer reactions

Phases and phase components

Spear (1981) performed hydrothermal phase equilibrium experiments on a mid-ocean ridge olivine tholeiite at a number of combinations of pressure, temperature, and oxygen fugacity. This study thus considers metamorphism of the same olivine tholeiite. Phases produced in the experiments include: hematite–ilmenite solid solution, clinopyroxene, orthopyroxene, olivine, quartz, sphene, plagioclase, amphibole (hornblende), pseudobrookite, and smectite. Pseudobrookite and smectite appeared in small quantities in only a few experimental products and therefore are not considered further. Spear also reported rather complete data on the composition of hornblendes in the experimental products as well as less complete data on pyroxene, plagioclase, ilmenite, and hematite composition.

In order to use phase composition to monitor reaction progress, the composition of the phases is first represented in terms of the scheme developed by Thompson et al. (1982) and Thompson (1982a). In this scheme the composition of each mineral phase is expressed as a single additive component in combination with a variety of exchange components. The components of the phases considered in this study are listed in Table 1. Following Thompson's (1982a) suggestion, the additive components are taken as simple end-member formulas. Seven exchange components, in addition, are necessary to account for the principle variations in mineral chemistry indicated by Spear's data. Exchange components that involve three or more atomic species have been given two-letter abbreviations consistent with those proposed by Thompson (1982a): ed = $NaAlSi_{-1}$; tk = $Al_2Mg_{-1}Si_{-1}$; and pl = $NaSiCa_{-1}Al_{-1}$. The components in Table 1 ignore the small amounts of Mn, K, and P which occur in some of the phases. The mid-ocean ridge tholeiite studied by Spear, however, contains only 0.18% K_2O, 0.18% MnO, and 0.15% P_2O_5; the small concentration of the three elements probably had a negligible affect on the phase equilibria and can be safely neglected. Phase components also ignore the small amount of Ti in pyroxene. The phase equilibrium experiments were conducted in the presence of an H_2–H_2O fluid; an additional phase which must be considered in the treatment of the metamorphism of the tholeiite therefore is an O–H fluid (Table 1).

Phase composition

The composition of quartz and sphene in the experiments is assumed to be fixed and equivalent to the additive components listed in Table 1 for the two minerals. Hematite and ilmenite solid solutions have compositions represented by a combination of Fe_2O_3 and $TiFe_{-1}$, where $X_{TiFe_{-1}} = X_{FeTiO_3}$. Plagioclase solid solutions have compositions represented by a combination of $CaAl_2Si_2O_8$

Table 1. Phases in metamorphosed mafic igneous rock and components used to describe their chemical composition

Phase	Additive component(s)	Exchange component(s)
hematite/ilmenite	Fe_2O_3	$TiFe_{-1}$
clinopyroxene	$CaMgSi_2O_6$	$FeMg_{-1}$, $MgCa_{-1}$, $FeAl_{-1}$, ed, tk, pl
orthopyroxene	$CaMgSi_2O_6$	$FeMg_{-1}$, $MgCa_{-1}$, $FeAl_{-1}$, tk
olivine	Mg_2SiO_4	$FeMg_{-1}$
quartz	SiO_2	--
sphene	$CaTiSiO_5$	--
plagioclase	$CaAl_2Si_2O_8$	pl
amphibole	$Ca_2Mg_5Si_8O_{22}(OH)_2$	$TiFe_{-1}$, $FeMg_{-1}$, $MgCa_{-1}$, $FeAl_{-1}$, ed, tk, pl
fluid	H_2O, H_2	--

and pl, where $X_{pl} = X_{ab} = 1 - X_{an}$. The compositions of hematite, ilmenite, and plagioclase therefore can be directly related to compositional parameters for the three minerals reported by Spear. Olivine solid solutions have compositions represented by Mg_2SiO_4 and $FeMg_{-1}$, where $X_{FeMg_{-1}} = 2X_{fa}$. Spear reported no olivine compositions; olivine composition was estimated from reported orthopyroxene composition and the experimental data on Fe–Mg partitioning between olivine and orthopyroxene of Medaris (1969).

The composition of hornblende must be represented by a combination of a single additive component and all of the exchange components. Thompson (1982a, Table 3b) presents a transformation of components which converts amphibole composition in terms of cations per 24 oxygen atoms into mole fraction of the seven exchange components. The component transformation was applied to Spear's data on amphibole composition (his Table 3); results are compiled in Table 2A of this report. Table 2C

presents a component transformation which converts pyroxene composition in terms of cations per six oxygen atoms to mole fraction of six exchange components, and was derived following procedures described by Thompson (1982a). The component transformation in Table 2C was applied to Spear's data on pyroxene composition (his Table 5); results are compiled in Table 2B of this report. The composition of clinopyroxene must be represented by a combination of an additive component and five of the exchange components. The composition of orthopyroxene may be adequately described without consideration of the components $TiFe_{-1}$, pl, and ed.

Net-transfer reactions

The composition of the fluid-rock system of Spear's experiments may be adequately described by these system components: Na_2O, CaO, FeO, MgO, Fe_2O_3, Al_2O_3, SiO_2, TiO_2, and H_2O (very small amounts of MnO, K_2O, and P_2O_5, as mentioned above, are ignored for simplicity). There are thus $c_s = 9$ system components. From Table 1, there are a total of $c_p = 30$ phase components. Following the treatment of Thompson (1982b), chemical reaction in the system may be fully described by $n_r = c_p - c_s = 21$ linearly independent reactions. The 21 reactions may be divided into two groups: (a) n_{ex} exchange reactions which involve exchange components only (e.g., $FeMg_{-1}$(amphibole) = $FeMg_{-1}$(clinopyroxene)) and (b) n_{nt} net-transfer reactions which involve two or more additive components and which may or may not also involve exchange components. By inspection of Table 1, there are $n_{ex} = 13$ linearly independent exchange reactions among the exchange components. The number of linearly independent net-transfer reactions therefore is $n_{nt} = n_r - n_{ex} = 21 - 13 = 8$. There is a wide latitude in which eight net-transfer reactions may be chosen as the set; the sole constraint is that they be linearly independent. One set is listed in Table 3. The reactions in Table 3 must be linearly independent because each reaction involves the single additive component of a different mineral phase (note that the additive components of orthopyroxene and clinopyroxene have the same formulas; they are different, however, because they refer to two different phases). An additional reason for formulating the net-transfer reactions as in Table 3 is that creation or destruction of each mineral phase is controlled by one and only one net-transfer reaction. All mass transfer among minerals and fluid in the experimental fluid-rock system can be thoroughly described by the 13 exchange reactions and the 8 net-transfer reactions in Table 3. The exchange reactions change the composition of participating phases and their relative modal abundance, but they in no way change the number of moles of fluid or mineral species present. Only the net-transfer reactions are capable of creating new minerals or changing the amounts of existing minerals. The net-transfer reactions, however, may also change the compositions of phases.

Table 2. Concentrations of exchange components in amphibole (A) and pyroxene (B) at various P–T–fo_2 conditions. C. Relation between the concentration of exchange components in pyroxene and the number of cations per six oxygen atoms.

Buffer	P(bars)	T(°C)	$X_{FeMg_{-1}}$	$X_{FeAl_{-1}}$	$X_{MgCa_{-1}}$	X_{pl}	X_{ed}	X_{tk}	$X_{TiFe_{-1}}$
				A. Amphibole composition					
HM	1000	650	0.47	0.42	0.15	0.17	0.18	0.72	0.04
HM	1000	706	0.43	0.42	0.38	0.04	0.24	0.57	0.05
HM	1000	754	0.45	0.43	0.46	0.14	0.20	0.69	0.05
HM	1000	883	0.31	0.60	0.35	0.26	0.39	0.94	0.15
QFM	1000	599	1.62	0.41	0.46	0.12	0.28	0.69	0.09
QFM	1000	651	1.51	0.38	0.47	0.12	0.35	0.70	0.08
QFM	1000	707	1.44	0.45	0.34	0.25	0.29	0.86	0.12
QFM	1000	750	1.35	0.51	0.26	0.23	0.31	0.88	0.15
QFM	1000	802	1.29	0.60	0.23	0.15	0.45	0.93	0.20
QFM	1000	850	1.22	0.68	0.10	0.29	0.37	1.14	0.24
HM	3000	701	0.47	0.52	0.18	0.18	0.32	0.71	0.08
HM	3000	752	0.49	0.52	0.12	0.23	0.23	0.89	0.07
HM	5000	698	0.58	0.60	0.20	0.18	0.27	0.98	0.08
QFM	3000	655	1.51	0.40	0.24	0.25	0.23	0.82	0.09
QFM	3000	763	1.41	0.51	0.24	0.19	0.36	0.88	0.15
				B. Pyroxene composition					
QFM	1000	850	0.35	0.03	0.24	0.00	0.01	0.04	—
QFM	1000	850	0.91	0.02	0.94	0.00	0.00	0.03	—
HM	1000	883	0.04	0.11	0.12	0.05	0.00	0.13	—

C. Component transformation for pyroxenes*

1. $X_{FeAl_{-1}} = Fe^{3+}$

2. $X_{FeMg_{-1}} = Fe^{2+}$

3. $X_{MgCa_{-1}} = 3 - \frac{1}{2}Na - \frac{1}{2}Fe^{3+} - \frac{1}{2}Al - Si - Ca$

4. $X_{tk} = Fe^{3+} + Al + Si - 2$

5. $X_{ed} = \frac{1}{2}Na + 2 - \frac{1}{2}Fe^{3+} - \frac{1}{2}Al - Si$

6. $X_{pl} = \frac{1}{2}Na + \frac{1}{2}Fe^{3+} + \frac{1}{2}Al + Si - 2$

*equations refer to cations per six oxygen atoms in pyroxene.

Table 3. Net-transfer reactions in metamorphosed mafic igneous rock

(1) $6 \text{ FeMg}_{-1} + 2 \text{ ed} + 2 \text{ MgCa}_{-1} + 3 \text{ H}_2\text{O} = \text{Fe}_2\text{O}_3 + 4 \text{ tk} + 2 \text{ pl} + 4 \text{ FeAl}_{-1} + 3 \text{ H}_2$

(2) $4 \text{ ed} + 3 \text{ MgCa}_{-1} + 12 \text{ FeMg}_{-1} + 6 \text{ H}_2\text{O} = \text{CaMgSi}_2\text{O}_6 \text{ (clinopyroxene)} + 4 \text{ pl} + 10 \text{ tk} + 12 \text{ FeAl}_{-1} + 6 \text{ H}_2$

(3) $4 \text{ ed} + 3 \text{ MgCa}_{-1} + 12 \text{ FeMg}_{-1} + 6 \text{ H}_2\text{O} = \text{CaMgSi}_2\text{O}_6 \text{ (orthopyroxene)} + 4 \text{ pl} + 10 \text{ tk} + 12 \text{ FeAl}_{-1} + 6 \text{ H}_2$

(4) $3 \text{ ed} + 3 \text{ MgCa}_{-1} + 8 \text{ FeMg}_{-1} + 4 \text{ H}_2\text{O} = \text{Mg}_2\text{SiO}_4 + 3 \text{ pl} + 7 \text{ tk} + 8 \text{ FeAl}_{-1} + 4 \text{ H}_2$

(5) $\text{ed} + 4 \text{ FeMg}_{-1} + \text{MgCa}_{-1} + 2 \text{ H}_2\text{O} = \text{SiO}_2 + \text{pl} + 3 \text{ tk} + 4 \text{ FeAl}_{-1} + 2 \text{ H}_2$

(6) $\text{TiFe}_{-1} + 3 \text{ ed} + 9 \text{ FeMg}_{-1} + 2 \text{ MgCa}_{-1} + 5 \text{ H}_2\text{O} = \text{CaTiSiO}_5 + 8 \text{ FeAl}_{-1} + 3 \text{ pl} + 7 \text{ tk} + 5 \text{ H}_2$

(7) $5 \text{ ed} + 16 \text{ FeMg}_{-1} + 4 \text{ MgCa}_{-1} + 8 \text{ H}_2\text{O} = \text{CaAl}_2\text{Si}_2\text{O}_8 + 5 \text{ pl} + 12 \text{ tk} + 16 \text{ FeAl}_{-1} + 8 \text{ H}_2$

(8) $13 \text{ MgCa}_{-1} + 15 \text{ ed} + 46 \text{ FeMg}_{-1} + 24 \text{ H}_2\text{O} = \text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2 + 15 \text{ pl} + 38 \text{ tk} + 46 \text{ FeAl}_{-1} + 23 \text{ H}_2$

Measurement of reaction progress with phase composition

General statement

In order to characterize metamorphism of mafic igneous rocks in the manner proposed, it is sufficient to monitor only the creation and destruction of minerals with changing physical conditions. Consequently the progress of the 13 exchange reactions was ignored, and only the net-transfer reactions were considered. The progress of net-transfer reactions can be measured from the modes of rocks. Unfortunately, Spear reports calculated modes for only a fraction of his experimental products. Consequently a method was developed by which progress of the net-transfer reactions was monitored by the composition of phases in the experimental products; it generalizes certain equations first presented by Thompson et al. (1982). The method also has application both to experimental studies involving the partial melting of rocks and to studies of isochemical suites of natural metamorphic rocks because most workers obtain the compositions of coexisting phases but rarely do they obtain modes.

Phase composition as a monitor of reaction progress

The method requires knowing the mineralogy and proportions of minerals in a single sample equilibrated at an arbitrary set of physical conditions. For this study the sample equilibrated at 1000 bars, 599°C, and f_{O_2} of the quartz–fayalite–magnetite (QFM) buffer was chosen as the reference. According to Figure 14 of Spear (1981), its mode is: hornblende (56%), plagioclase (41%), and ilmenite (3%). Using molar volume data from Robie et al. (1967) and the mineral composition data of Spear, 1000 cm^3 of such rock contains approximately 2.026 moles amphibole, 4.082 moles plagioclase, and 0.951 moles ilmenite. Using 1000 bars, 599°C, QFM as a reference point, the net-transfer reactions were calculated which 1000 cm^3 of such rock would experience as physical conditions were changed to the other P–T–f_{O_2} conditions at which Spear performed experiments (specifically those listed in Table 2). The calculations involved simulta-

neously solving a set of mass balance equations of the form:

$$\sum_j X^{\circ}_{i,j} n^{\circ}_j + \sum_k \nu_{i,k} \xi_k = \sum_j X^{f}_{i,j} \left(n^{\circ}_j + \sum_k \nu_{j,k} \xi_k \right) \quad (1)$$

where the subscripts i, j, and k refer to exchange components, mineral phases or their additive components, and the different net-transfer reactions, respectively. The ξ_k's are the desired values of reaction progress in units of moles/1000 cm^3 rock. ξ_k for each of the k = 1–8 net-transfer reactions in Table 3 may be formally defined as the number of moles of additive mineral component produced (+) or consumed (−) by the kth net-transfer reaction. $X_{i,j}$ is the mole fraction of component i in phase j; $\nu_{i,k}$ is the stoichiometric coefficient of exchange component i in the kth net-transfer reaction (positive for products and negative for reactants), $\nu_{j,k}$ is the stoichiometric coefficient of additive mineral component j in the kth net-transfer reaction (always positive), and n_j is the number of moles of mineral phase j. Superscript ° refers to initial conditions before reaction; superscript f refers to final conditions after reaction. Each equation (1) simply states that the number of moles of exchange component i in the system before reaction plus the number of moles of component i produced by reaction is equal to the number of moles of i after reaction. Equation (1) is the generalized form of equation (26) of Thompson et al. (1982).

Values of the mole fractions that appear in equation (1) were taken from the following sources: amphiboles and pyroxenes—Table 2; hematite, ilmenite, and plagioclase—Spear (1981, Table 3); olivine—calculated from orthopyroxene composition as described previously. Quartz and sphene were considered pure substances fixed in composition. Composition data for hematite, ilmenite, plagioclase, and pyroxene were not reported for all P–T–f_{O_2} conditions. In these cases, the following default values were chosen: hematite, $X_{\text{TiFe}_{-1}} = 0.24$; ilmenite, $X_{\text{TiFe}_{-1}} = 0.90$; plagioclase, $X_{\text{pl}} = 0.50$; clinopyroxene at f_{O_2} of the QFM buffer, first pyroxene analysis, Table 2B; orthopyroxene, second pyroxene analysis, Table 2B; clinopyroxene at f_{O_2} of the hematite–magnetite (HM) buffer, third pyroxene analysis, Table 2B. The

Table 4. Sample calculation of reaction progress from phase composition. Example refers to reaction which would occur in 1000 cm³ mafic rock between 1000 bars; 599°C; QFM and 1000 bars; 883°C; HM.

Exchange component	Mass balance equation
$TiFe_{-1}$	$0.09(2.026) + 0.9(0.951) = 0.15(2.026 + \xi_8) + 0.24(0.951 + \xi_1)$
pl	$0.12(2.026) + 0.5(4.082) + 2\xi_1 + 4\xi_2 + \xi_5 + 5\xi_7 + 15\xi_8 = 0.26(2.026 + \xi_8) + 0.58(4.082 + \xi_1) + 0.05\xi_2$
ed	$0.28(2.026) - 2\xi_1 - 4\xi_2 - \xi_5 - 5\xi_7 - 15\xi_8 = 0.39(2.026 + \xi_8)$
$FeMg_{-1}$	$1.62(2.026) - 6\xi_1 - 12\xi_2 - 4\xi_5 - 16\xi_7 - 46\xi_8 = 0.31(2.026 + \xi_8) + 0.04\xi_2$
$MgCa_{-1}$	$0.46(2.026) - 2\xi_1 - 3\xi_2 - \xi_5 - 4\xi_7 - 13\xi_8 = 0.35(2.026 + \xi_8) + 0.12\xi_2$

Solution: Because neither the initial nor final sample contains orthopyroxene, olivine, or sphene, $\xi_3 = \xi_4 = \xi_6 = 0$.

Solving the above five equations simultaneously, $\xi_1 = +2.874$; $\xi_2 = +2.667$; $\xi_5 = +3.681$; $\xi_7 = -0.293$;

$\xi_8 = -1.225$.

default values are not greatly different from the compositions of mineral phases in any of the experimental products.

Because the initial or reference sample contains amphibole, ilmenite, and plagioclase, all solutions involved ξ_1, ξ_7, and ξ_8. For every additional mineral phase that occurs in the final sample, an additional net-transfer reaction is involved in the mineral–fluid reaction which relates the two states, and an additional ξ must be solved for. For every mineral phase that appears neither in the initial reference sample nor in the final sample, the progress of the appropriate net-transfer reaction in Table 3 was set at zero. Thus the set of equations that were used to solve for the ξ's contained a number of equations exactly equal to the number of different minerals that occur in either the initial reference sample or the final sample or both (hematite and ilmenite were considered different compositions of the same mineral solid solution). For the transition from the reference state to either 1000 bars, 902°C, HM or to 1000 bars, 912°C, QFM, one of the equations was $\xi_8 = -2.026$ (amphibole disappears from the experimental charges with increasing temperature at these physical conditions). Table 4 illustrates a sample calculation that refers to the transition from 1000 bars, 599°C, QFM to 1000 bars, 883°C, HM. No calculation involved more than five equations of the form of equation (1). The sample calculation in Table 4 lists the five exchange components that were chosen to formulate the mass balance equations. Equations involving the exchange components tk and $FeAl_{-1}$ did not give good solutions, perhaps because the ferric iron content of the amphiboles was only approximately determined. When fewer than five exchange components were required to obtain a solution, the components chosen were in the same priority as the order in which they are listed in Table 4.

Results

Table 5 lists calculated results. The calculations correctly predict the phase assemblage in samples at each of the final P–T–f_{O_2} states with just three exceptions. The solution for $P = 1000$ bars, $T = 802°C$, QFM predicts no clinopyroxene while clinopyroxene is reported in the run products; the solution for $P = 1000$ bars, $T = 850°C$, QFM predicts no olivine while a trace of olivine is reported in the run products; the solution for $P = 3000$ bars, $T = 752°C$, HM predicts no sphene while sphene is reported in the run products. The discrepencies might be explained by one or more of the following: (a) errors in the chemical analysis of the mineral phases; (b) error in the assumed phase compositions used in the solutions (clinopyroxene, 752°, 802°; hematite, 752°); (c) lack of complete chemical equilibrium among the mineral phases in the sample; and/or (d) the amount of clinopyroxene in the sample equilibrated at 802°C, the amount of olivine in the sample equilibrated at 850°C, and the amount of sphene in the sample equilibrated at 752°C is indeed very small. Judging from data in Spear's Appendix A, explanation (d) is the most probable reason why olivine did not appear in the solution for 1000 bars; 850°C; QFM. In support of this conclusion, the small value of ξ_2 in Table 5 for 3000 bars; 752°C; HM is consistent with only a trace of clinopyroxene in the sample as is reported by Spear (his Appendix A).

Because there are more exchange components than ξ's, the system of equations like (1) is actually overdetermined and a least-squares solution could be obtained. Least-squares solutions, however, were not sought because trial calculations involving the components tk and $FeAl_{-1}$ produced results which were at odds with Spear's experimental results (i.e., the solutions predicted appearance of a mineral phase when experiment indicated the

Table 5. Calculated values of the progress of net-transfer reactions in mafic igneous rock for the P–T–fo_2 interval between 1000 bars, 599°C, QFM and the conditions listed in the lefthand three columns of each entry. Values of reaction progress refer to a quantity of rock with volume 1000 cm³ at 1000 bars, 599°C, QFM.

Buffer	P(bars)	T(°C)	ξ_1	ξ_2	ξ_3	ξ_4	ξ_5	ξ_6	ξ_7	ξ_8
HM	1000	650	+2.160	0	0	0	+1.756	+0.298	+0.549	−0.626
HM	1000	706	+2.527	0	0	0	+1.793	0	+0.900	−0.739
HM	1000	754	+3.875	+2.674	0	0	+2.607	0	+0.469	−1.529
HM	1000	883	+2.874	+2.667	0	0	+3.681	0	−0.293	−1.225
HM	1000	902	+3.375	+4.775	0	0	+2.993	0	+0.423	−2.026
QFM	1000	651	+0.012	0	0	0	0	0	−0.394	+0.118
QFM	1000	707	−0.108	0	0	0	0	0	−0.900	+0.307
QFM	1000	750	−0.193	0	0	0	0	0	−1.007	+0.350
QFM	1000	802	−0.116	(0)	+1.692	0	0	0	+0.835	−0.715
QFM	1000	850	−0.170	+0.873	+2.053	(0)	0	0	+0.028	−0.760
QFM	1000	912	+0.154	+3.073	+0.900	+2.756	0	0	+1.298	−2.026
HM	3000	701	+1.608	0	0	0	+2.745	+0.300	+0.071	−0.476
HM	3000	752	+3.060	+0.018	0	0	+1.351	(0)	+1.391	−0.945
HM	5000	698	+0.927	0	0	0	+2.657	+0.406	−0.431	−0.233
QFM	3000	655	−0.023	0	0	0	0	0	−0.685	+0.235
QFM	3000	763	−0.150	0	0	0	0	0	−0.245	+0.089

phase disappeared or vice versa). Because errors in the mineral compositions used in the calculations are not well known, no attempt was made to assess the uncertainty associated with each of the calculated values of reaction progress in Table 5.

Calculated modes

Using the amounts of minerals in the reference sample (equilibrated at 1000 bars; 599°C; QFM), the net-transfer reactions in Table 3, and the calculated progress of the reactions (Table 5), the identity and amounts of minerals in samples equilibrated at the other P–T–fo_2 conditions listed in Table 6 were calculated from the relation:

$$n_j^f = n_j^\circ + \sum_k \nu_{j,k}\xi_k \qquad (2)$$

summed over the k net-transfer reactions. Amounts of minerals were converted to volumes of minerals using molar volume data (Robie et al., 1967) and reported

Table 6. Calculated modes of metamorphosed mafic igneous rock*

Buffer	P(bars)	T(°C)	Hem/Ilm	Cpx	Opx	Oliv	Qz	Sph	Plag	Am
HM	1000	650	9(6)	0	0	0	4(2)	2(2)	47(45)	38(45)
HM	1000	706	11(9)	0	0	0	4(3)	0	50(46)	35(42)
HM	1000	754	15(9)	18(11)	0	0	6(2)	0	47(46)	14(32)
HM	1000	883	12(9)	18(11)	0	0	9(3)	0	39(45)	22(32)
HM	1000	902	14(10)	32(34)	0	0	7(4)	0	47(52)	0
QFM	1000	599	3(3)	0	0	0	0	0	41(41)	56(56)
QFM	1000	651	3(3)	0	0	0	0	0	37(39)	60(58)
QFM	1000	707	3(3)	0	0	0	0	0	32(37)	65(60)
QFM	1000	750	3(3)	0	0	0	0	0	31(36)	66(61)
QFM	1000	802	3(2)	0(4)§	11(5)	0	0	0	50(40)	36(49)
QFM	1000	850	3(2)	6(6)	13(6)	0(3)§	0	0	42(42)	36(41)
QFM	1000	912	4(3)	21(17)	6(23)	13(11)	0	0	56(46)	0
HM	3000	701	8	0	0	0	6	2	42	42
HM	3000	752	12	0.1	0	0	3	§	55	30
HM	5000	698	6	0	0	0	6	2	37	49
QFM	3000	655	3	0	0	0	0	0	34	63
QFM	3000	763	3	0	0	0	0	0	39	58

*Am = amphibole; Sph = sphene; Hem = hematite; Ilm = ilmenite; Plag = plagioclase; Qz = quartz; Cpx = clinopyroxene; Opx = orthopyroxene; Oliv = olivine. Modes reported by Spear (1981) for P = 1000 bars in parentheses.
§reported in experimental products but not produced by calculated reactions.

compositions of the mineral phases. Volume amounts, normalized to 100%, correspond to modes, and these are listed in Table 6. Modes calculated for samples equilibrated at 1000 bars agree very well with those calculated by Spear from the composition of the mineral phases and the composition of the starting material of the experiments.

Applications: the model metamorphism of mafic igneous rock

General statement

Calculated values of ξ in Table 5 form the basis for quantitative models of the metamorphism of mafic igneous rock. Six model metamorphic processes or environments will be characterized and discussed: (1) isobaric metamorphism with increasing temperature at fo_2 buffered by both the QFM and HM buffers; (2) isothermal metamorphism with increasing pressure at buffered fo_2; (3) metamorphism along a geothermal gradient of 7.4°C/km at buffered fo_2; (4) metamorphism along a geothermal gradient of 22°C/km at buffered fo_2; (5) isobaric, isothermal oxidation; and (6) isobaric oxidation with increasing temperature. Each of the metamorphic environments will be characterized in terms of prograde mineral reactions, changes in modes, changes in rock volume, kinds and amounts of volatile species consumed or released, P–V work performed by the rock on its environment or vice versa, and the interaction of mafic rocks with external heat and fluid reservoirs during metamorphism.

Isobaric metamorphism with increasing temperature at buffered oxygen fugacity

Experiments performed at 1000 bars pressure with increasing temperature, serve as a model of contact metamorphism at a depth of 3–4 km in the crust. Two models of contact metamorphism are considered: one for fo_2 equivalent to that of the QFM buffer and the other for fo_2 equivalent to the HM buffer.

Mineral reactions. The overall mineral reaction that the mafic rock used in Spear's experiments undergoes during the transition between any two of the P–T–fo_2 states listed in Table 5 is:

$$\sum_k \left[\sum_j \nu_{j,k}(j) \right] (\xi_k^f - \xi_k^o) = 0 \qquad (3)$$

with the values of $\nu_{j,k}$ taken from Table 3, the values of ξ_k taken from Table 5, superscript ° referring to the initial state, and superscript f referring to the final state after reaction. Results for reactions at 1000 bars between 599°C and 912°C at fo_2 of the QFM buffer and between 650°C and 902°C at fo_2 of the HM buffer are presented in Table 7. Exchange components have been omitted from the reactions in Table 7 in order to highlight which minerals and fluid species are created and destroyed. All reactions in Table 7 refer to a quantity of rock which occupies 1000

cm^3 at 599°C and 1000 bars under conditions of the QFM buffer.

At conditions of the QFM buffer the model rock is composed at 599°C of amphibole, ilmenite, and plagioclase. Amphibole initially is produced with increasing temperature at the expense of plagioclase ± ilmenite. At a temperature between 750°C and 802°C amphibole reacts to orthopyroxene, ilmenite, and plagioclase. With further increase in temperature, orthopyroxene and clinopyroxene are products while plagioclase and ilmenite join amphibole as reactants. Between 850°C and 912°C orthopyroxene and amphibole are reactants while ilmenite, plagioclase, clinopyroxene, and olivine are products. Above 912°C the rock no longer contains amphibole; reaction progress could not be monitored further because Spear reported no experimental data above 912°C. The reaction sequence apparently is quite complicated and not necessarily what one might predict simply from a knowledge of the equilibrium mineral assemblage at each temperature.

At conditions of the HM buffer, the model rock is composed initially at 650°C of amphibole, sphene, quartz, hematite, and plagioclase. With increasing temperature, amphibole and sphene react to produce hematite, plagioclase, and quartz. After sphene is completely consumed, amphibole and plagioclase react to form hematite, quartz, and clinopyroxene. Between 754°C and 883°C, plagioclase, hematite, and a very small amount of clinopyroxene react to form amphibole. Finally between 883°C and 902°C amphibole is consumed through reaction with quartz to produce hematite, clinopyroxene, and plagioclase. Oxygen fugacity obviously has a profound influence on the mineral phases which appear in the rock during contact metamorphism. As under conditions of the QFM buffer, the prograde reaction sequence is complicated.

Change in modes. The change in rock mode during isobaric contact metamorphism at buffered oxygen fugacity is illustrated in Figure 1 (data compiled from Table 6). The calculated changes in rock mode with increasing temperature reflect the prograde reactions described previously.

Change in rock volume. During the transition between any two P–T–fo_2 states in Table 5 the overall mineral-fluid reaction may cause a change in rock volume. The final rock volume was calculated by converting the amounts of minerals in a sample after reaction into volumes of minerals, as described previously, and summing together the volumes of minerals. The calculation of rock volume assumes that metamorphic rock contains negligible porosity during its crystallization and that volatiles produced by the mineral reactions leak away from the rock shortly after they are generated. Results for model isobaric contact metamorphism are presented in Figure 2. Rock volume decreases with increasing temperature because the devolatilization reactions which occur during metamorphism are generally characterized

Table 7. Overall mineral–fluid reaction which occurs in mafic igneous rocks as physical conditions change between the two sets of physical conditions listed in the lefthand six columns of each entry (exchange components omitted). Reactions refer to a quantity of rock with volume 1000 cm³ at 1000 bars; 599°C; QFM.*

P^o	T^o	B^o	P^f	T^f	B^f	Overall mineral-fluid reaction
						Isobaric increase in temperature, buffered oxygen fugacity
1000	599	QFM	1000	651	QFM	$0.394Plag + 0.413H_2 = 0.012Ilm + 0.118Am + 0.295H_2O$
1000	651	QFM	1000	707	QFM	$0.121Ilm + 0.505Plag + 0.048H_2 + 0.141H_2O = 0.189Am$
1000	707	QFM	1000	750	QFM	$0.085Ilm + 0.107Plag + 0.121H_2 = 0.043Am + 0.078H_2O$
1000	750	QFM	1000	802	QFM	$1.066Am = 0.077Ilm + 1.692Opx + 1.842Plag + 0.608H_2 + 0.458H_2O$
1000	802	QFM	1000	850	QFM	$0.053Ilm + 0.807Plag + 0.045Am + 0.244H_2 = 0.873Cpx + 0.361Opx + 0.288H_2O$
1000	850	QFM	1000	912	QFM	$1.153Opx + 1.266Am + 0.673H_2 = 0.323Ilm + 2.200Cpx + 2.756Oliv + 1.270Plag + 1.939H_2O$
1000	650	HM	1000	706	HM	$0.298Sph + 0.113Am + 0.097H_2 = 0.367Hem + 0.036Qz + 0.352Plag + 0.209H_2O$
1000	706	HM	1000	754	HM	$0.431Plag + 0.789Am = 1.347Hem + 2.674Cpx + 0.815Qz + 0.112H_2 + 0.678H_2O$
1000	754	HM	1000	883	HM	$1.000Hem + 0.007Cpx + 0.763Plag + 0.012H_2 + 0.291H_2O = 1.074Qz + 0.304Am$
1000	883	HM	1000	902	HM	$0.688Qz + 0.801Am = 0.501Hem + 2.109Cpx + 0.716Plag + 0.082H_2 + 0.719H_2O$
						Isothermal increase in pressure, buffered oxygen fugacity
1000	706	HM	3000	701	HM	$0.919Hem + 0.829Plag + 0.325H_2O = 0.952Qz + 0.300Sph + 0.263Am + 0.062H_2$
3000	701	HM	5000	698	HM	$0.681Hem + 0.088Qz + 0.503Plag + 0.103H_2 + 0.141H_2O = 0.107Sph + 0.244Am$
						Geothermal gradient = 7.4°/km, buffered oxygen fugacity
1000	599	QFM	3000	655	QFM	$0.024Ilm + 0.685Plag + 0.154H_2 + 0.080H_2O = 0.235Am$
						Geothermal gradient = 22°/km, buffered oxygen fugacity
1000	599	QFM	3000	763	QFM	$0.150Ilm + 0.245Plag + 0.369H_2 = 0.089Am + 0.280H_2O$
						Isobaric, isothermal oxidation
3000	763	QFM	3000	752	HM	$0.801Ilm + 1.034Am + 0.711H_2O = 4.011Hem + 0.018Cpx + 1.350Qz + 1.636Plag + 1.745H_2$
1000	651	QFM	1000	650	HM	$0.963Ilm + 0.744Am + 0.988H_2O = 3.111Hem + 1.756Qz + 0.298Sph + 0.943Plag + 1.922H_2$
1000	850	QFM	1000	883	HM	$0.781Ilm + 2.053Opx + 0.321Plag + 0.465Am + 1.217H_2O = 3.825Hem + 1.794Cpx + 3.681Qz + 1.681H_2$
1000	912	QFM	1000	902	HM	$1.105Ilm + 0.900Opx + 2.756Oliv + 0.876Plag + 2.437H_2O = 4.327Hem + 1.703Cpx + 2.993Qz + 2.437H_2$
						Isobaric oxidation with increase in temperature
1000	599	QFM	1000	754	HM	$0.951Ilm + 1.529Am = 4.826Hem + 2.674Cpx + 2.608Qz + 0.469Plag + 1.476H_2 + 0.053H_2O$
1000	599	QFM	1000	883	HM	$0.951Ilm + 1.225Am + 0.293Plag + 0.239H_2O = 3.825Hem + 2.667Cpx + 3.681Qz + 1.464H_2$
1000	599	QFM	1000	902	HM	$0.951Ilm + 2.026Am = 4.326Hem + 4.776Cpx + 2.993Qz + 0.423Plag + 1.546H_2 + 0.480H_2O$

*See footnote to Table 6 for phase notation.
P^o = initial pressure (bars); P^f = final pressure (bars); T^o = initial temperature (°C); T^f = final temperature (°C); B^o = initial f_{O_2} buffer; B^f = final f_{O_2} buffer.

by a negative change of volume of solids. The fully anhydrous mafic rocks at temperatures above 900°C occupy a volume 3–4% less than the hydrous amphibolites from which they evolved at 600–650°C.

Evolved volatiles. During the transition between any two P–T–fo_2 points in Table 5, mineral–fluid reactions will release or consume the volatile species H_2O and H_2. The molar amount of fluid species released (+) or consumed (−) per 1000 cm³ rock may be calculated from:

$$n_j^f = \sum_k \nu_{j,k}(\xi_k^f - \xi_k^o) \qquad (4)$$

where species j refers either to H_2O or H_2. Cumulative moles volatiles involved in the model prograde contact metamorphism, calculated from equation (4), are plotted in Figure 3 as a function of temperature. Reactions at conditions both of the QFM and HM buffers release a net amount of 1.3–2.9 moles H_2O. More H_2O is released at conditions of the QFM buffer, in part, because the mafic rock initially contains more amphibole under conditions of the QFM buffer. Mineral–fluid reactions on the QFM buffer consume approximately one cumulative mole H_2 between 600°C and 912°C, a phenomenon not usually included in conventional treatments of prograde mineral
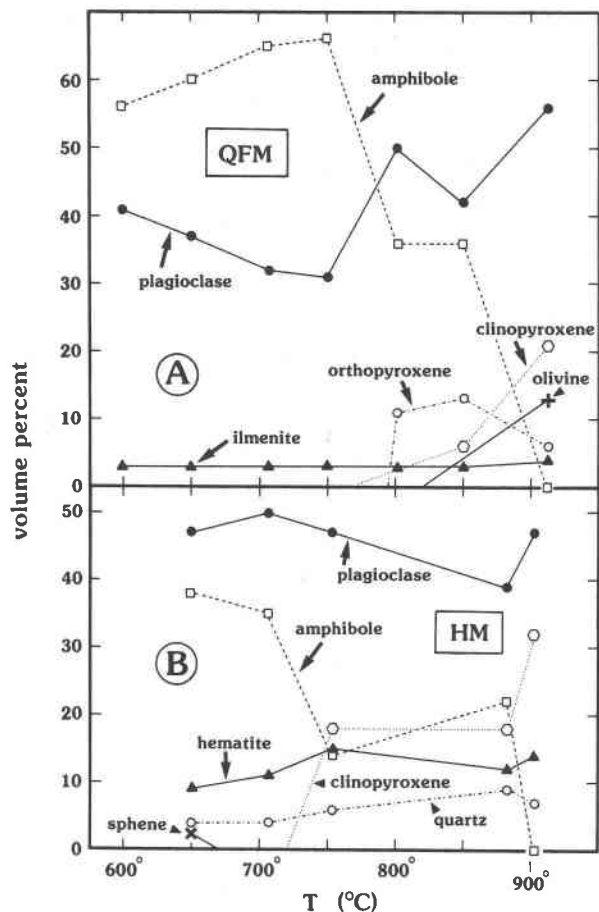
Fig. 1. Calculated modes of metamorphosed mafic igneous rock at 1000 bars as a function of temperature. A. fo_2 defined by the QFM buffer; B. fo_2 defined by the HM buffer.

reactions in mafic schists. Because the model mafic rock is anhydrous at temperatures above 912°C, H_2 consumed by reaction is released as H_2O. Even though metamorphism proceeded at fo_2 buffered by the QFM buffer, the rock was nevertheless reduced during the prograde reac-
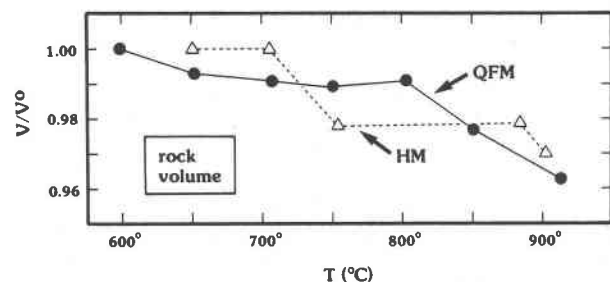

Fig. 2. Calculated cumulative change in volume of metamorphosed mafic igneous rock at 1000 bars pressure as a function of temperature. V is rock volume at temperature, $V°$ is rock volume at 599°C for model metamorphism on the QFM buffer and at 650°C for metamorphism on the HM buffer.
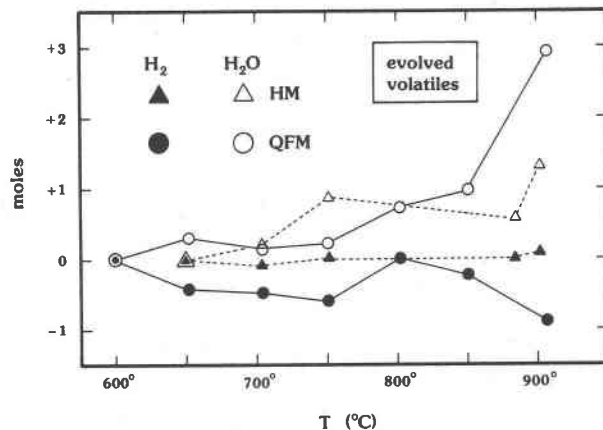

Fig. 3. Cumulative moles volatiles released (+) or consumed (−) during metamorphism of mafic igneous rock at 1000 bars pressure as a function of temperature and oxygen fugacity. Number of moles volatiles refers to a quantity of rock with volume 1000 cm^3 at 1000 bars, 599°C, QFM.

tion sequence. In retrospect, the reduction of mafic rock with increasing temperature under conditions of the QFM buffer could have been predicted from the lower thermal stability of amphibole under conditions of the HM buffer than under conditions of the QFM buffer (F. S. Spear, pers. comm., 1983). In contrast, there was essentially no net gain or loss of H_2 by the model rock metamorphosed on the HM buffer. The reason for the difference in behavior of the mafic rock under the two different oxidation states is the composition of the coexisting aqueous fluid. The mole fraction of hydrogen in fluid coexisting with rock at the HM buffer was ≪0.0001 at 1000 bars and 600–900°C; the small concentration of hydrogen in the fluid precludes any significant exchange of the species between rock and fluid. The mole fraction of H_2 in O–H fluid at conditions of the QFM buffer in the same range of pressure and temperature is 0.002–0.01; the larger concentration of hydrogen in the fluid permits exchange of the species between rock and fluid. (The species composition of O–H fluid was calculated from data in Ohmoto and Kerrick, 1977, or Hewitt, 1978, assuming ideal mixing and using fugacity coefficients for H_2O and H_2 from Burnham et al., 1969 and Ryzhenko and Volkov, 1971, respectively). The consumption of H_2 by reactions on the QFM buffer and its later release as H_2O also explains why the mafic rock released over twice as much H_2O during metamorphism under conditions of the QFM buffer than was released by reactions on the HM buffer.

P–V work. The amount of *P–V* work performed by mafic rock on its surroundings (or vice versa) during the model metamorphic event may be calculated from:

$$W = -P\left[\Delta V_r + \sum_k \nu_{H_2O,k}(\xi_k^f - \xi_k^o)\overline{V}_{H_2O} + \sum_k \nu_{H_2,k}(\xi_k^f - \xi_k^o)\overline{V}_{H_2}\right] \quad (5)$$

Table 8. Compounds whose enthalpies were used to estimate the enthalpies of the exchange components.

Exchange component	Compounds used to estimate enthalpies of exchange components	Source of enthalpy data
$FeMg_{-1}$	$CaFeSi_2O_6 - CaMgSi_2O_6$	Helgeson et al. (1978)
$MgCa_{-1}$	$2\ MgSiO_3 - CaMgSi_2O_6$	Helgeson et al. (1978)
$FeAl_{-1}$	$\frac{1}{2}(Fe_2O_3 - Al_2O_3)$	Helgeson et al. (1978)
$TiFe_{-1}$	$FeTiO_3 - Fe_2O_3$	Robie et al. (1978)
pl	$NaAlSi_3O_8 - CaAl_2Si_2O_8$	Helgeson et al. (1978)
ed	$NaAlSi_3O_8 - 4\ SiO_2$	Helgeson et al. (1978)
tk	$NaCa_2Mg_4Al_3Si_6O_{22}(OH)_2 + 4\ SiO_2 - Ca_2Mg_5Si_8O_{22}(OH)_2 - NaAlSi_3O_8$	Helgeson et al. (1978)

with the change in rock volume, ΔV_r, calculated as described previously and the values of $\nu_{j,k}$ and ξ_k from Tables 3 and 5, respectively. Molar volumes of H_2O were taken from Burnham et al. (1969); molar volumes for H_2 were calculated from the modified Redlich–Kwong equation of state of Holloway (1981). Molar volumes of fluid species were entered as those at the midpoint of the $P-T$ interval considered. Equation (5) implies a momentary retention of volatiles, generated by mineral reaction, within mafic rock during metamorphism. This behavior of fluid superficially differs from the behavior of fluid assumed in the calculation of change in rock volume and therefore deserves further explanation. Change in rock volume (Fig. 2) was calculated assuming that fluid generated by mineral reactions leaks from the rock shortly after it is generated. Leakage, however, requires a finite time and the instant that the volatiles are generated, they remain in the rock. The amount of $P-V$ work associated instantaneously with mineral reaction therefore was calculated considering momentary retention of volatiles generated within the rock and hence using the change in volume of both mineral and fluid phases due to reaction. Equation (5) provides an estimate of the cumulative amount of $P-V$ work instantaneously performed by the rock on its surroundings or vice versa during a given interval of reaction progress, $\xi_k^f - \xi_k^\circ$. The equation does not, however, consider any $P-V$ work which might occur as volatiles, produced within the rock, leak off. Calculated values of $P-V$ work may be significant because they represent a quantitative measure of the hydrofracture potential of rock undergoing mineral reaction. Negative values of W indicate the conversion of chemical work into mechanical ($P-V$) work which, if of sufficient magnitude, could fracture the rock undergoing reaction. The fractures would then provide avenues for the escape of fluid from the rock (cf. Walther and Orville, 1982). Calculated values of $P-V$ work may be useful in understanding the mechanisms by which volatiles escape from rock during metamorphic events.

The cumulative amount of $P-v$ work involved in iso-

baric metamorphism between 600° and 912°C under conditions of both the QFM and HM buffers is plotted against T in Figure 4. On the QFM buffer, approximately 1000 cal $P-V$ work was initially performed on the mafic rock by its surroundings. Between 750° and 912°C, however, the rock did approximately 4000 cal work on its surroundings; a net amount of $P-V$ work was therefore performed by the rock. A net 1900 cal $P-V$ work was performed by the mafic rock during model metamorphism under conditions of the HM buffer between 650°C and 900°C. The smaller amount of $P-V$ work performed under the more oxidizing conditions is simply a reflection of the less intense devolatilization that the rock experienced on the HM buffer compared to conditions on the QFM buffer (Fig. 3).

Heat budget. The amount of heat absorbed or released by the mafic rock during metamorphism (Q_T) may be calculated from:

$$Q_T = C_P(T^f - T^\circ) + \sum_k \Delta \overline{H}_k^{P,T} (\xi_k^f - \xi_k^\circ) \qquad (6)$$

where C_P is heat capacity and $\Delta \overline{H}^{P,T}$ is the enthalpy of reaction k at the $P-T$ conditions of the reaction. The terms of $(T^f - T^\circ)$ and $(\xi_k^f - \xi_k^\circ)$ refer to the difference in the variables between any two $P-T-fo_2$ conditions listed in Table 5. The value of C_P was calculated for the amphibole–plagioclase–ilmenite rock at 1000 bars, 599°C, QFM from data in Robie et al. (1978) and was assumed to be constant over the range in P and T discussed in this paper (0.808 cal/cm^3–°C). Values of $\Delta \overline{H}_k^{P,T}$ were calculated from data of Helgeson et al. (1978), Robie et al. (1978), and Burnham et al. (1969), and refer to $P-T$ conditions at the midpoint of the two $P-T-fo_2$
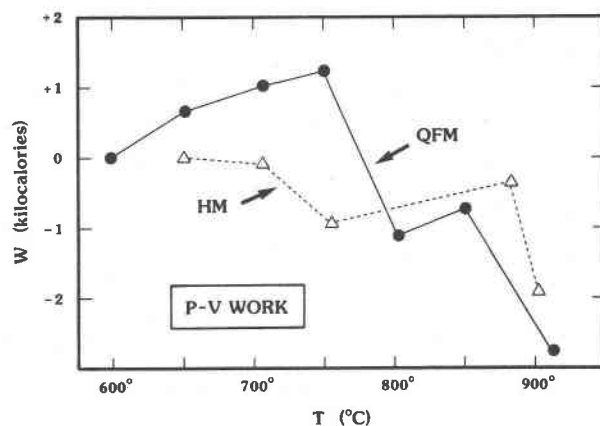

Fig. 4. Cumulative $P-V$ work performed by mafic igneous rock on its environment ($-$) or vice versa ($+$) during metamorphism at 1000 bars as a function of temperature and oxygen fugacity. Amount of work refers to a quantity of rock with volume 1000 cm^3 at 1000 bars, 599°C, QFM. The value of W was set to 0 at 599°C for model metamorphism on the QFM buffer and at 650°C for metamorphism on the HM buffer.

Table 9. Estimated enthalpies of selected exchange reactions of $P = 1$ bar and $T = 1000$ K.

Exchange reaction	$\Delta \bar{H}^{1 \text{ bar, } 1000^{\circ}\text{K}}_{\text{(cal)}}$
$\frac{1}{2}Fe_2SiO_4 + MgSiO_3 = \frac{1}{2}Mg_2SiO_4 + FeSiO_3$ $FeMg_{-1}(\text{olivine}) = FeMg_{-1}(\text{orthopyroxene})$	730
$MgSiO_3 + CaMgSiO_4 = CaSiO_3 + Mg_2SiO_4$ $MgCa_{-1}(\text{pyroxene/pyroxenoid}) = MgCa_{-1}(\text{olivine})$	1078
$\frac{1}{2}Ca_3Al_2Si_3O_{12} + Ca_2FeAl_2Si_3O_{12}(OH) = \frac{1}{2}Ca_3Fe_2Si_3O_{12} + Ca_2Al_3Si_3O_{12}(OH)$ $FeAl_{-1}(\text{epidote}) = FeAl_{-1}(\text{garnet})$	2697[†]
$2SiO_2 + NaAl_3Si_3O_{10}(OH)_2 = NaAlSiO_4 + Al_2Si_4O_{10}(OH)_2$ $\text{ed(dioctahedral sheet silicate)} = \text{ed(nepheline/tridymite)}$	5764[*]
$Ca_2Al_2SiO_7 + CaMgSi_2O_6 = Ca_2MgSi_2O_7 + CaAl_2SiO_6$ $\text{tk(akermanite/gehlenite)} = \text{tk(clinopyroxene)}$	6611
$Fe_3O_4 + FeTiO_3 = Fe_2TiO_4 + Fe_2O_3$ $TiFe_{-1}(\text{rhombohedral oxide}) = TiFe_{-1}(\text{spinel})$	6644[§]
$CaAl_2Si_2O_8 + NaAlSi_2O_6 = NaAlSi_3O_8 + CaAl_2SiO_6$ $\text{pl(clinopyroxene)} = \text{pl(feldspar)}$	8661

*†reaction metastable above 700°K. *reaction metastable above 800°K; calculated using data for quartz=tridymite from Robie et al. (1978). §from Spencer and Lindsley (1981).*

states which enter into calculations using equation (6). The enthalpies of the exchange components in reactions (1)–(8), Table 3, were estimated as the difference between the enthalpies of the various compounds listed in Table 8. Table 9 lists enthalpies of exchange reactions, involving each of the seven exchange components in Table 1, calculated for $P = 1$ bar, $T = 1000$°K from data in Helgeson et al. (1978) (except where noted). Tabulated values are 0.7–8.7 kcal compared to enthalpies of net-transfer reactions (1)–(8), Table 3, which are in the range of 49.6–616.4 kcal at 1 bar, 1000°K. Not all reactions in Table 9 are directly applicable to phases that occur in metamorphosed mafic igneous rocks (thermodynamic data for minerals is limited). Nevertheless the values of $\Delta \bar{H}$ listed in Table 9 can probably be taken as good evidence that the enthalpies of exchange reactions are negligible compared to those of the net-transfer reactions. The exchange reactions were therefore ignored in the calculations of the heat budgets of the model metamorphic events. The cumulative amount of heat involved in isobaric metamorphism between 599°C and 912°C under conditions of both the QFM and HM buffers is plotted as a function of temperature in Figure 5. Not surprisingly, the overall model prograde metamorphic event involves absorption of heat by the mafic rock from its surroundings. The net amount of heat absorbed, approximately 300 cal/cm³ rock between 599°C and 912°C, is dominated by the $C_P\Delta T$ term in equation (6). Under conditions of the QFM buffer only approximately 10% of the total, cumula-

tive heat budget is used to drive prograde mineral reactions; under conditions of the HM buffer, the proportion is 8%. The behavior of mafic rocks differs greatly from that of pelitic schists and impure carbonate rocks during metamorphism. Approximately 40% of the metamorphic
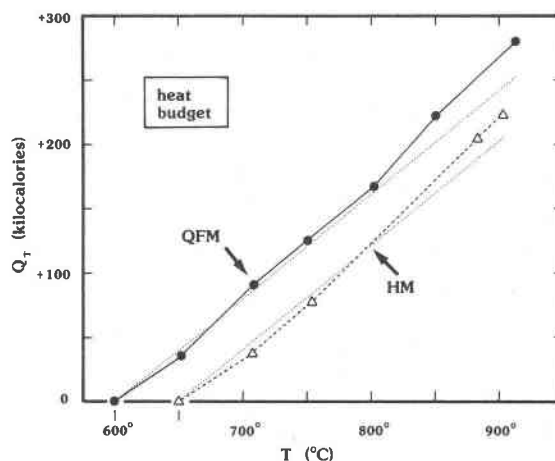

Fig. 5. Cumulative heat absorbed by mafic igneous rock from its environment during metamorphism at 1000 bars as a function of temperature and oxygen fugacity. Amount of heat refers to a quantity of rock with volume 1000 cm³ at 1000 bars, 599°C, QFM. Dotted lines refer to the cumulative $C_P\Delta T$ contribution to Q_T for each oxygen fugacity. The value of Q_T was set to 0 at 599°C for model metamorphism on the QFM buffer and at 650°C for metamorphism on the HM buffer.

Table 10. Final rock volume, moles volatiles evolved or consumed, heat absorbed or released, P–V work, and volume of H_2O fluid involved in metamorphism of mafic igneous rock between the two sets of physical conditions listed in the lefthand seven columns of each entry.*

P^o	T^o	B^o	V_r^o	P^f	T^f	B^f	V_r^f	n_{H_2O}	n_{H_2}	Q_T	W	V_{H_2O}
*Isothermal increase in pressure, buffered oxygen fugacity*
1000	706	HM	1002	3000	701	HM	1002	−0.325	+0.062	+19.2	+404	--
3000	701	HM	1002	5000	698	HM	1002	−0.141	−0.103	+14.0	+709	--
*Geothermal gradient = 7.4°/km, buffered oxygen fugacity*
1000	599	QFM	1000	3000	655	QFM	995	−0.080	−0.154	+53.1	+726	--
*Geothermal gradient = 22°/km, buffered oxygen fugacity*
1000	599	QFM	1000	3000	763	QFM	995	+0.280	−0.369	+128.5	+703	--
*Isobaric, isothermal oxidation*
3000	763	QFM	995	3000	752	HM	1002	−0.711	+1.745	−50.1	−4254	14,700
1000	651	QFM	993	1000	650	HM	1002	−0.988	+1.922	−17.2	−2986	18,200
1000	850	QFM	977	1000	883	HM	981	−1.217	+1.681	+3.0	−1838	15,500
1000	912	QFM	963	1000	902	HM	972	−2.437	+2.437	−39.1	−1228	22,900
*Isobaric oxidation with increase in temperature*
1000	599	QFM	1000	1000	754	HM	979	+0.053	+1.476	+96.0	−2803	13,900
1000	599	QFM	1000	1000	883	HM	981	−0.239	+1.464	+226.8	−2514	13,600
1000	599	QFM	1000	1000	902	HM	972	+0.480	+1.546	+243.3	−3734	14,300

*P^o = initial pressure (bars); P^f = final pressure (bars); T^o = initial temperature (°C); T^f = final temperature (°C); B^o = initial f_{O_2} buffer; B^f = final f_{O_2} buffer; V_r^o = initial rock volume (cm^3); V_r^f = final rock volume (cm^3); n_{H_2O} = moles H_2O evolved (+) or consumed (−); n_{H_2} = moles H_2 evolved (+) or consumed (−); Q_T = heat absorbed (+) or released (−) (kcal); W = P–V work performed by rock on its surroundings (−) or vice versa (+) (cal); V_{H_2O} = volume of H_2O required to oxidize rock (cm^3). All extensive quantities refer to a quantity of rock with volume 1000 cm^3 at conditions P = 1000 bars; T = 599°C; f_{O_2} defined by the QFM buffer.

heat budget of pelitic rocks is used to drive the prograde mineral reactions (Walther and Orville, 1982) while 75–90% of the heat budget drives mineral reactions during metamorphism of impure carbonate rocks (Ferry, 1983a). The enthalpy of a reaction is positively correlated with the number of moles volatile species evolved (Walther and Orville, 1982). The difference in behavior of amphibolites, therefore, is likely a consequence of their smaller volatile content compared to pelitic schists and metacarbonate rocks. The volatile content of greenschists, however, is larger than that of amphibolites and the percentage of a mafic rock's heat budget used to drive mineral reactions might be much larger than 10% at metamorphic temperatures below 600°C, particularly at the transition from greenschist to amphibolite facies conditions.

Isothermal metamorphism with increasing pressure at buffered oxygen fugacity

Experiments at approximately 700°C; 1000, 3000, and 5000 bars pressure; and under conditions of the HM buffer model isothermal metamorphism which might occur, for example, shortly after the emplacement of a thick, cold thrust sheet or a pile of cold nappes. The overall prograde mineral reaction which would occur during the transition from 1000 bars to 5000 bars pressure is listed in Table 7; data in Table 6 indicate the corresponding change in rock mode. Table 10 lists the changes in rock volume which would occur as well as the number of moles of volatiles consumed and released, and the amount of heat and P–V work associated with prograde mineral–fluid reaction. All values in Tables 6, 7, and 10 were calculated using equations (2)–(6) as discussed previously.

During isothermal metamorphism induced by increasing pressure, the mafic rock develops amphibole + sphene±quartz at the expense of plagioclase and hematite±quartz. Although the reaction is endothermic, a small net amount of H_2O is consumed. Rock volume remains essentially unchanged. Because the overall prograde reaction involves hydration, P–V work is done on the rock by its environment.

Metamorphism along a geothermal gradient at buffered oxygen fugacity

Calculated results under conditions of the QFM buffer at (a) 599°C, 1000 bars; (b) 655°C, 3000 bars; and (c)

763°C, 3000 bars were used to model prograde metamorphism of mafic igneous rock along two geothermal gradients. The difference between P–T conditions (a) and (b) corresponds to a geothermal gradient of approximately 7.4°C/km and models the high-pressure facies series metamorphism that occurs, for example, in subducted oceanic crust. The difference between P–T conditions (a) and (c) corresponds to a geothermal gradient of approximately 22°C/km and models the intermediate-pressure facies series of "normal" regional metamorphism. The overall mineral reactions, changes in modes, changes in rock volume, amounts of volatiles evolved or consumed, and the amount of heat and P–V work involved in model metamorphism of mafic igneous rock along each of the two geothermal gradients are summarized in Tables 6, 7, and 10.

Metamorphism along the 7.4°C/km gradient is qualitatively similar to isothermal metamorphism with increasing pressure: the overall mineral reaction produces amphibole at the expense of plagioclase, Fe–Ti oxide, and H_2O; rock volume changes negligibly; P–V work is done on the rock by its surroundings; and a small amount of heat is absorbed by the rock from its surroundings.

Metamorphism along the 22°C/km gradient is qualitatively similar to model isobaric contact metamorphism in the temperature range 599–750°C: the overall mineral reaction creates amphibole from plagioclase and ilmenite; much heat is absorbed by the rock from its environment; and P–V work is performed on the rock by its surroundings.

Isothermal, isobaric oxidation

Calculated results at (a) ~750°C, 3000 bars; (b) ~650°C, 1000 bars; (c) ~850°C, 1000 bars; and (d) ~900°C, 1000 bars under conditions of both the QFM and HM buffers models isobaric and approximately isothermal oxidation of metamorphosed mafic igneous rock. Isothermal, isobaric oxidation of rock might occur, for example, during some instances of hydrothermal alteration. Tables 6, 7, and 10 list mineral–fluid reactions; changes in rock mode; changes in rock volume; moles volatiles released and consumed; and amounts of heat and P–V work involved in model oxidation of mafic rock. The overall reaction that occurs during oxidation of amphibole-bearing rocks is similar at the three different temperatures investigated: amphibole and ilmenite are replaced by hematite and quartz±clinopyroxene±plagioclase±sphene. In every reaction oxidation of rock is accomplished by consumption of H_2O by the mineral reaction and release of H_2 by the rock to its surroundings. Reactions may be either exothermic or slightly endothermic, but all involve P–V work done by the rock on its environment. Rock volume increases by less than 1%.

The oxidation reactions in Table 7 can be used along with calculated concentrations of species in O–H fluid in equilibrium with metamorphosed mafic igneous rock to quantitatively estimate the amount of fluid involved in oxidation of rock. The calculation assumes a model reaction mechanism by which rock is oxidized through its interaction with oxidizing O–H fluid. The fluid before interaction with rock has composition of an O–H fluid in equilibrium with hematite + magnetite at the P–T conditions of reaction (i.e., $X_{H_2} = \sim 0$). Both seawater and meteoric water would be examples of geologically meaningful aqueous fluids with $X_{H_2} = \sim 0$. The fluid after interaction with rock is assumed to be an O–H fluid in equilibrium with quartz + fayalite + magnetite at the P–T conditions of reaction ($X_{H_2} = 0.002$–0.01 depending on P and T). The volume of oxidizing fluid required to drive the calculated oxidation reaction (V_{H_2O}) may be determined from the following equation:

$$X_{H_2} = \frac{\sum_k \nu_{H_2,k}(\xi_k^f - \xi_k^o)}{\sum_k (\nu_{H_2,k} + \nu_{H_2O,k})(\xi_k^f - \xi_k^o) + V_{H_2O}/\overline{V}_{H_2O}^{P,T}} \tag{7}$$

where $\overline{V}_{H_2O}^{P,T}$ is the molar volume of H_2O at the P–T conditions of the reaction (from Burnham et al., 1969), $\nu_{H_2O,k}$ and $\nu_{H_2,k}$ are the stoichiometric coefficients of H_2O and H_2 in the oxidation reactions (from Table 3), X_{H_2} refers to the concentration of hydrogen in fluid in equilibrium with the mafic rock under conditions of the QFM buffer (calculated as discussed previously), and $(\xi_k^f - \xi_k^o)$ refers to the difference in ξ between the four pairs of P–T–f_{O_2} conditions investigated. The calculation assumes that f_{O_2} is fixed at the value defined by QFM throughout rock oxidation. During actual oxidation of mafic rock, f_{O_2} would change during mineral–fluid reaction from that of QFM to that defined by HM. The X_{H_2} of fluid in equilibrium with rock would therefore decrease with progress of the reaction. Consequently volumes of fluid calculated by equation (7) represent *minimum* estimates of the amount of fluid required to oxidize ~1000 cm³ metamorphosed mafic igneous rock. More accurate estimates of fluid volumes could be obtained if the relation between f_{O_2} and reaction progress during oxidation were known, but this information cannot be extracted from Spear's experimental data. Results calculated from equation (7) are presented in the right-hand column of Table 10. Observed degrees of oxidation require interaction of mafic rock with at least 14.7–22.9 rock volumes H_2O fluid. The model calculations presented here emphasize that the measured progress of oxidation reactions in natural metamorphosed mafic igneous rocks may have important applications in monitoring water-rock interaction during hydrothermal alteration (e.g., Ferry, 1983b).

Isobaric oxidation with increasing temperature

Comparison of calculated results at 599°C, QFM with those at (a) 754°C, HM; (b) 883°C, HM; and (c) 902°C, HM describes oxidation of metamorphosed mafic igneous rock with an isobaric increase in temperature at 1000 bars

pressure. Oxidation of rock with an increase in temperature at 1000 bars models fluid–rock interaction during shallow-level (3–4 km depth) contact metamorphism which involves circulation of heated, oxidizing, meteoric water through the aureole (cf., Taylor, 1974). The overall prograde mineral–fluid reactions; changes in rock mode; changes in rock volume; moles fluid species consumed and evolved; and the amount of heat and P–V work involved in model prograde oxidation/metamorphism of mafic rock are summarized in Tables 6, 7, and 10. The change in mode of the mafic rock is qualitatively similar to the change associated with isothermal, isobaric oxidation. Model prograde metamorphism involves absorption of much heat by the rock from its surroundings and P–V work performed by the rock on its environment. The reactions in Table 7 reveal that the mechanism of oxidation is evolution of H_2 by the rock during reaction with little release or consumption of H_2O. The H_2 released by the mafic rock in nature would be carried away by a metamorphic fluid. Because the concentration of H_2 in O–H fluids is small, a substantial amount of fluid is required. If the metamorphic fluid were an O–H fluid that contained no H_2 before fluid–rock interaction (e.g., it was in equilibrium with hematite + magnetite) and contained an amount of H_2 after reaction corresponding to equilibrium with quartz + fayalite + magnetite, then the volume of fluid needed to accomplish the oxidation may be calculated using equation (7). Values for the intensive variables in equation (7) were chosen as appropriate for the midpoint of the temperature interval in which reaction proceeded in the three cases investigated. Calculated results appear in the right-hand column of Table 10 and, as mentioned previously, represent minimum estimates of the actual amount of fluid required to oxidize $\sim$1000 cm^3 metamorphosed mafic igneous rock. According to this model, calculated degrees of oxidation with increasing temperature require the participation of at least 13.6–14.3 rock volumes O–H fluid depending on the temperature interval considered. Calculated results indicate that the measured progress of oxidation/dehydration reactions in contact metamorphosed rocks may act as extremely sensitive monitors of fluid-rock interaction in the crust and could serve as a useful complement to geochemical studies involving the stable isotopes of hydrogen and oxygen.

Conclusions

The change in mineral composition observed in metamorphosed mafic igneous rocks acts as a quantitative record of the progress of the prograde mineral–fluid reactions that occurred during their metamorphic evolution. Measured values of reaction progress, in turn, can be used to determine the mineral reactions, changes in mode, changes in rock volume, identity and amount of volatile species released or consumed, and the amount of P–V work associated with the metamorphism of individ-

ual rock samples. Perhaps more importantly, measurement of reaction progress allows quantitative characterization of the way in which rocks interact with external heat and fluid reservoirs during metamorphism. Measured values of reaction progress, therefore, have important applications in determining the amount and pattern of mass and energy transfer which occurs in the crust during metamorphic events. The model calculations presented in this study indicate what kinds of heat-rock and fluid–rock interactions are likely to occur during high-temperature metamorphism of mafic igneous rock in a variety of metamorphic environments. Although calculations were based on laboratory phase equilibrium studies, they are equally applicable not only to investigations of natural mafic metamorphic rocks but also to metamorphic rocks of other bulk compositions.

Acknowledgments

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