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BUFFERING OF PORE FLUIDS BY METAMORPHIC REACTIONS

H. J. GREENWOOD

Department of Geological Sciences,
University of British Columbia, Vancouver 8, B.C., Canada

ABSTRACT. During the progressive metmorphism of many carbonates and pelites, it may be more reasonable to assume that the mineralogy has controlled the composition of the fluid phase rather than the more commonly assumed converse. The view that the minerals may buffer the fluid is supported by calculations that demonstrate the conditions under which such buffering can operate. For rocks in which buffering operates, the most conspicuous changes in mineral assemblages should occur at isobaric invariant points, to which the composition of the fluid has been driven by the buffering process. From the standpoint of mapping isograds in metamorphosed rocks, the polybaric traces of isobaric invariant points may be regarded as the best candidates for isograd boundaries, rather than the related isobaric univariant equilibria. In iron bearing rocks the oxygen fugacity is ordinarily controlled by the mineralogy rather than being imposed externally and thus should not be regarded as an *independent* variable.

INTRODUCTION

The complexity of modern experimental and theoretical phase diagrams is difficult to reconcile with the fact that field studies of metamorphic terranes usually give a rather simple and repeatable sequence of observed mineral reactions or isograds. If representations of mineral equilibria such as the $\log_{10} f_{O_2}$ versus T, the log f_i versus log f_j, the μ_i versus μ_j, or the T-x_{CO_2} diagram are to be taken at face value, then there should be a bewildering number of possible sequences to observe and little hope of making any simple sense out of a field area. The fact remains, however, that some order prevails. This paper seeks to resolve the apparent difficulty by proposing that the mineral reactions in many rocks are capable of buffering the composition of the pore fluids in contrast to the common assumption that the pore fluids control the mineralogy.

THEORY

Part of the complexity of the phase relations between metamorphic minerals is due to the separation of variables for purposes of thermodynamic analysis and graphical representation. Variables such as f_{O_2}, f_{S_2}, f_{H_2}, f_{H_2O}, f_{CO_2}, mole fractions such as x_{CO_2}, and of course pressure and temperature are usually separated from one another whenever possible. This is both because of simplicity in graphical representation and because variation of free energy is an exact differential, making such separation thermodynamically legal and convenient. However, it is possible that in many natural situations some of these variables are not separable, depending one on the other through buffering by various mineral reactions. In this case it is impossible arbitrarily to impose, for example, both x_{CO_2} and temperature on a carbonate-silicate assemblage, as the imposition of temperature will cause reactions that directly control the composition of the fluid. It seems possible, therefore, that the separation of variables referred to above may be an excellent device for the experi-

mentalist and the theoretician but a potentially misleading one for those who would interpret natural mineral assemblages.

The first question to be answered is, therefore, the extent of reaction required for the mineral assemblages to buffer the fluid, and for this we will examine first some equilibria involving two volatile constituents such as H_2O and CO_2, and which are usually illustrated on isobaric diagrams of T versus x_{CO_2}.

Now, since

$$x_2 = \frac{n_2}{n_1 + n_2}$$

we have

$$\frac{dx_2}{dn_2} = \frac{1 - x_2\left(1 + \frac{dn_1}{dn_2}\right)}{n_1 + n_2}$$

Further, both constituents 1 and 2 may be involved in the reaction contributing n_1 and n_2 to the fluid phase, so we have also

$$\frac{dn_1}{dn_2} = \frac{\nu_1}{\nu_2}$$

where ν_1 and ν_2 are the stoichiometric coefficients of components 1 and 2 in the reaction (positive for products, negative for reactants). To simplify,

let

$$A = \frac{\nu_1 + \nu_2}{\nu_2} \qquad (\nu_2 \neq 0)$$

giving

$$\frac{dx_2}{dn_2} = \frac{1 - Ax_2}{n_1 + n_2} \tag{1}$$

As n_1 and n_2 are coupled we can write

$$n_1 - n_1^\circ = (n_2 - n_2^\circ)\frac{dn_1}{dn_2}$$

where n_1° and n_2° are the initial quantities of components 1 and 2 in the system. This permits integration to

$$\frac{1 - Ax_2}{1 - Ax_2^\circ} = \frac{n_1^\circ + n_2^\circ}{n_1^\circ + n_2^\circ + A(n_2 - n_2^\circ)} \quad (\nu_2 \neq 0) \tag{2}$$

which can be simplified by setting $n_1^\circ + n_2^\circ = 1$
to

$$x_2 = \frac{n_2}{1 + A(n_2 - n_2^\circ)} \qquad (\nu_2 \neq 0) \tag{3}$$

or

$$n_2 = \frac{x_2(1 - An_2^\circ)}{1 - Ax_2} \qquad (\nu_2 \neq 0) \tag{4}$$

The restriction $\nu_2 \neq 0$ can be removed by noting the symmetry of the mole fraction coordinate, changing x_2 for x_1 and ν_1 for ν_2. These equations give the composition of the fluid phase as it evolves by reaction with a mineral equilibrium, starting with one mole of fluid containing n_2° moles of component 2 and progressing to a state with n_2 moles of component 2 at a composition x_2.

Equations 3 and 4 are illustrated in figures 1 through 4. Figure 1 shows the evolution of fluids buffered by reactions with $\nu_1 = -1$, $\nu_2 = +1$, such as magnesite + H_2O = brucite + CO_2. Several paths are shown, each with the same slope as demanded by equation 1. For example, if pure H_2O were buffered by such a reaction the path followed would be given by the curve labelled $n_2^\circ = 0$, and the distance travelled would be limited by the location of the equilibrium composition for the temperature and pressure in question. Each starting composition would follow its own path. Figure 2 illustrates the evolution of a fluid buffered by reaction with $\nu_1 = 0$, $\nu_2 = 1$, such as calcite + quartz = wollastonite + CO_2. It applies equally well to a reaction with $\nu_1 = 1$, $\nu_2 = 0$, if the diagram is reversed. For the diagram as shown, a fluid consisting initially of 0.8 moles H_2O and 0.2 moles CO_2 would follow the curve $n_2^\circ = 0.2$ if buffered by a reaction producing only CO_2. It will be noticed that if one starts with essentially pure H_2O in such a situation the buffering capacity of the mineral reaction is initially as good as that shown in figure 1. As reaction proceeds, the capacity of the reaction to affect the fluid composition becomes progressively less, until eventually the composition $x_2 = 1$ is approached asymptotically. Fluids that begin with some of component 2 in them already are less easily buffered than those that start with none. Figure 3 illustrates the evolution of fluids buffered by a reaction with $\nu_1 = 1$, $\nu_2 = 1$, such as for the example 2 talc + 3 calcite = tremolite + dolomite + CO_2 + H_2O. The interpretation is as with figures 1 and 2, but note that the composition of the asymptote is now at $x_2 = 0.5$, corresponding to the composition of the fluid evolved by the reaction. The buffering capacity is initially almost as good as in figure 2, but it is much more rapidly lost as reaction progresses toward the asymptotic composition. Figure 4 illustrates the same process for buffering by a reaction with $\nu_1 = 1$, $\nu_2 = 3$, such as for example the metastable reaction talc + 3 calcite + 2 quartz = 3 diopside + H_2O + $3CO_2$. As in figure 3 the fluid composition asymptotically approaches the composition of the evolved fluid, in this case at $x_2 = 0.75$.

Figures 2 through 4 show that the buffering capacity of mineral reactions is greatest for fluids initially far removed in composition from the composition of the evolved fluid and for small extents of reaction. Naturally, if a smaller amount of fluid is present at the start a correspondingly smaller amount of reaction will be needed to effect the same degree of buffering. It is important now to examine some specific examples to see what magnitudes of Δx_2 and Δn_2 are needed to buffer one mole of fluid.

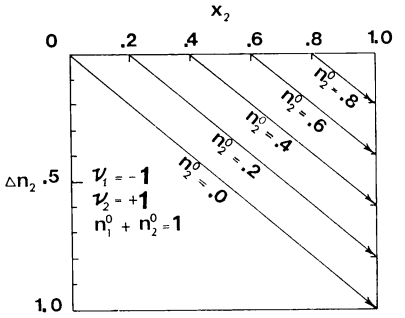

Fig. 1

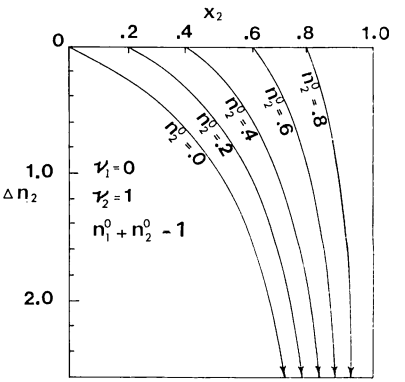

Fig. 2

Fig. 1. Evolution of 1 mole of a binary fluid due to buffering by a reaction with $\nu_1 = -1$, $\nu_2 = 1$. Initial points lie on the x_2 axis where $\Delta n_2 = 0$. Direction of evolution indicated by arrows. Example: magnesite + H_2O = brucite + CO_2. ν_1 and ν_2 are stoichiometric coefficients in the reaction.

Fig. 2. Evolution of 1 mole of a binary fluid due to buffering by a reaction with $\nu_1 = 0$, $\nu_2 = 1$. Initial points lie on the x_2 axis, and direction of evolution is shown by arrows. Note that the initial buffering effect is strong but decreases with reaction progress, asymptotically approaching pure component 2 ($x_2 = 1$). Such a reaction is an effective buffer only at low x_2. Example: calcite + quartz = wollastonite + CO_2. Reversal of the diagram makes it applicable to reactions where $\nu_1 = 1$, $\nu_2 = 0$.

EXAMPLES

Examples from systems involving H_2O and CO_2.—Figure 5 illustrates the relations at 2000 bars P_{fluid} pressure between the phases forsterite, magnesite, talc, serpentine, brucite, and periclase in a binary mixture of H_2O and CO_2 represented in a T-x diagram (Greenwood, 1967). The curves have been calculated from thermodynamic constants consistent with the experimental data of Walter, Wyllie, and Tuttle (1962), Johannes (1969), and Greenwood (1967). (See caption.)

The simplest example to choose at first involves only the phases brucite (B), magnesite (M), periclase (P), and fluid. Consider first the buffering of pure H_2O over to the most CO_2-rich part of the brucite field, invariant point [BMP]. From equation 4, if buffering takes place by the reaction M = P + CO_2 then $\Delta n_{CO_2} = 0.0805$ and if by reaction M + H_2O = B + CO_2 then $\Delta n_{CO_2} = 0.0745$. These figures are moles of CO_2 evolved per mole of initial fluid. Because of the stoichiometry of the reactions the numbers also give the moles of magnesite consumed in the process and the moles of mineral products formed.

We may now consider the "progressive metamorphism" of a magnesite rock, starting for example with one mole of fluid of composition $x_{CO_2} = 0.02$. Introduction of heat raises the temperature until the curve M + H_2O = B + CO_2 is reached at point "A" (530°C, 0.02). Further addition of heat raises the temperature and causes the reaction to proceed, consuming H_2O and producing CO_2 in the same proportions.

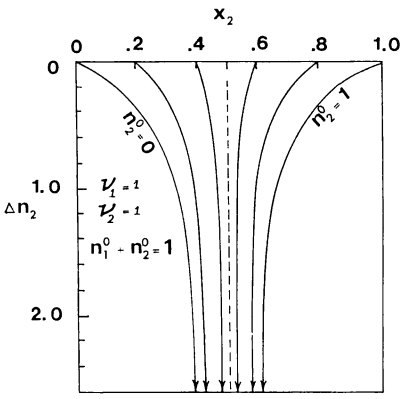

Fig. 3

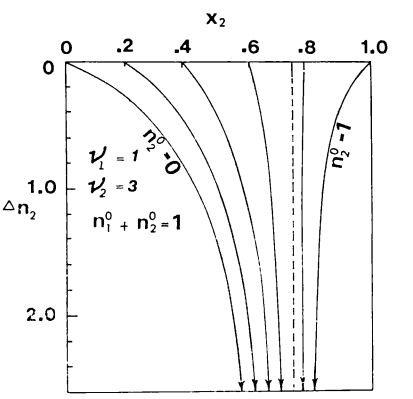

Fig. 4

Fig. 3. Evolution of 1 mole of a binary fluid due to buffering by a reaction with $\nu_1 = 1$, $\nu_2 = 1$. Composition of the fluid asymptotically approaches $x_2 = 0.5$, the composition of the fluid given off by the reaction. Buffering capacity lost more rapidly than in figure 2. Example: 2 talc + 3 calcite = tremolite + dolomite + H_2O + CO_2.

Fig. 4. Evolution of a binary fluid buffered by a reaction with $\nu_1 = 1$, $\nu_2 = 3$. Symbols and interpretations as in figures 1 through 3. See text. Example: talc + 3 calcite + 2 quartz = 3 diopside + H_2O + 3 CO_2.

The production of B by this process is, between point "A" and the invariant point, $\Delta n_B = \Delta n_{CO_2} = 0.0545$ according to equation 4. In terms of weight, this corresponds to a production of 3.17 g of brucite per mole of fluid. That is, passage of 18 g of fluid through 300 g of magnesite would produce only one percent of brucite in the process of buffering. It is unlikely that this amount of brucite would be observed petrographically, and although the rock was buffered completely over the range 530° to 644°C, evidence for this might easily be missed.

At invariant point [BMP] further addition of heat causes no increase in temperature as long as B and M are present at equilibrium with the fluid, the heat going entirely to promoting reactions

$$B = P + H_2O \qquad (R1)$$

and

$$M = P + CO_2. \qquad (R2)$$

These reactions combine to give off a fluid of invariant composition ($x_{CO_2} = 0.0745$) by proceeding in the proportions

$$\frac{R1}{R2} = \frac{0.9255}{0.0745} = 12.4$$

Clearly, the B produced to this point is minor in quantity, and the reaction destroying it (R1) must proceed much farther (by a factor of 12.4) than the reaction destroying M. When all B is gone and M + P remain, buffering will continue along the course of reaction R2. These relations are illustrated in figure 6, plotting grams of minerals versus

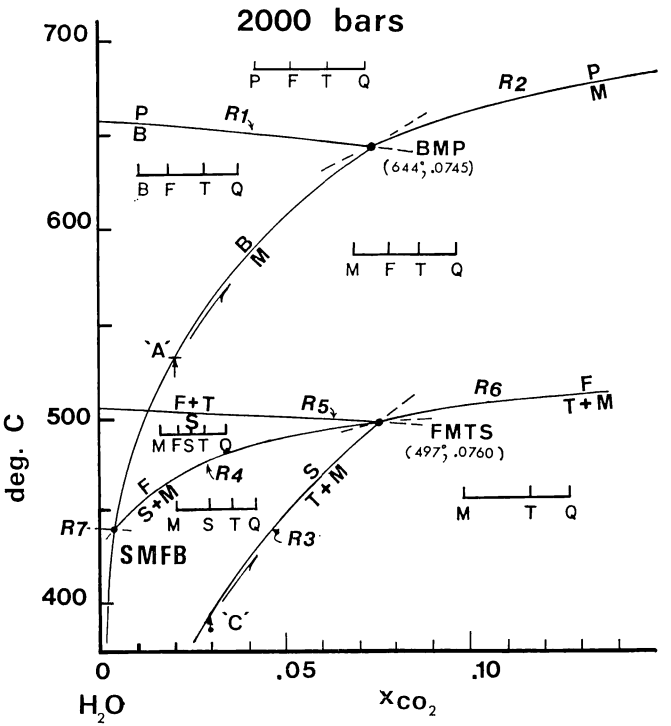

Fig. 5. Water-rich part of the 2-kb T-X_{CO_2} section for the system MgO–SiO_2–H_2O–CO_2. Diagram calculated assuming ideal mixing of CO_2 and H_2O, together with thermodynamic constants given below, consistent with the experimental work of Walter, Wyllie, and Tuttle (1962), Johannes (1969), and Greenwood (1967).

Reaction

(R1)	$B = P + H_2O$	ΔH(2kb) = 10.3 kcal,	T° = 657°C
(R2)	$M = P + CO_2$	ΔH(2kb) = 28.1 kcal,	T° = 830°C
(R5)	$5S = 2T + 12F + 18H_2O$	ΔH(2kb) = 12.5 kcal,	T° = 505°C
(R7)	$S + 2B = 4F + 2H_2O$	ΔH(2kb) = 10.5 kcal,	T° = 440°C

T° = equilibrium temperature in pure gas at 2 kb. ΔH(2kb) is given in kcal per mole of evolved gas at a total pressure of 2 kb. Points A and C are referred to in the text.

temperature, as weights are closer to petrographic observation than moles. The important features revealed, in addition to the fairly small amounts of brucite involved (3.17 g), are the gradual growth of B as the buffering proceeds toward the invariant point, followed by its abrupt disappearance and the equally abrupt appearance of 2.36 g of periclase.

The importance of this abrupt change of assemblage is that its abruptness may make it more readily observed than a gradual change and that it occurs at a definite temperature for this pressure, in contrast to the isobaric univariant equilibria. Consequently changes of this sort taking place at isobaric invariant points are more likely to be observed in rocks than those related to isobaric univariant reactions. The amounts

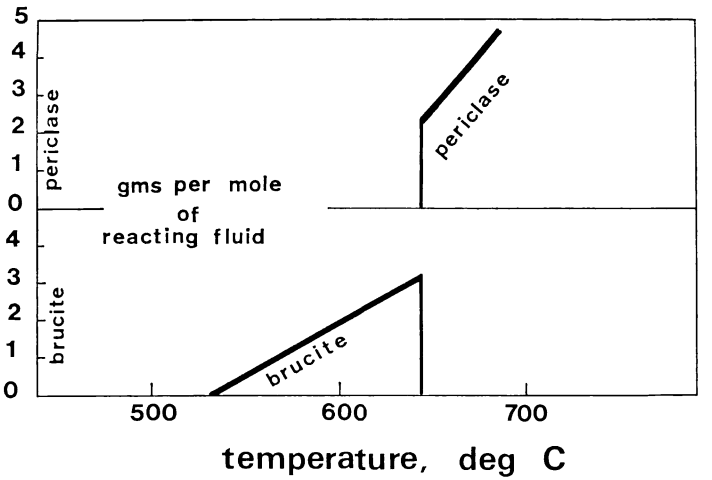

Fig. 6. Variation in abundance of brucite and periclase with increasing temperature in a system with fluid buffered by mineral reactions. The salient points are the gradual appearance of a small amount of brucite due to the reaction M + H_2O = B + CO_2 before reaching the invariant point [BMP] at 644°C and the sudden appearance of periclase at the expense of brucite upon passing the invariant point.

of brucite and periclase produced, however, are small and might go undetected, unless a large amount of fluid had reacted with the rock. The buffering process appears capable of driving the fluid composition to such isobaric invariant points, forcing the change to be observed at the same temperature for a wide range of bulk compositions. In the example just given, if we had started with a mixture of brucite and magnesite with the ratio M/B less than 0.0807, then M would have been consumed before B, with the buffering proceeding along the curve B = P + H_2O. It would not buffer far, however, as may be seen from equation 4 or figure 2 (mirror image).

A similar progression may be traced on figure 5 with the more complicated assemblages involving forsterite (F), talc (T), magnesite (M), serpentine (S), and fluid, which together define the invariant point [FMTS]. Let us begin, by way of example, with T + M at 395°C and x_{CO_2} = 0.03 (point C in fig. 5). By adding heat we raise the temperature to 497°C, [FMTS], and buffer the fluid by progress of reaction R3.

$$T + 3M + 3H_2O = S + 3CO_2 \qquad (R3)$$

This involves the evolution of CO_2, which by equation 4 is equal to Δn_{CO_2} = 0.046 moles CO_2 per mole of starting fluid. This will require a minimum of 0.046 moles M and a minimum of 0.015 moles T; otherwise, one or the other would be consumed before reaching [FMTS], with a resultant loss of buffering and possible intersection with reaction R4.

$$S + 2M = 4F + 4H_2O + 2CO_2 \qquad (R4)$$

For 95 percent of the possible range of T + M mixtures, therefore, both T and M will be sufficient, and the invariant point [FMTS] will be reached by the fluid, with the production of 0.015 moles of serpentine per mole of initial fluid. Behavior at the invariant point requires some discussion. Four reactions are possible, reactions R3 and R4 noted above, and reactions R5 and R6 noted below.

$$5S = 2T + 12F + 18H_2O \qquad (R5)$$

$$T + 5M = 4F + H_2O + 5CO_2 \qquad (R6)$$

In a non-equilibrium or near-equilibrium situation, the consumption of added heat by the four reactions would be determined by their relative reaction rates coupled with the requirement that the fluid evolved by the combined effects of all four reactions must be of invariant composition. All reactions would proceed in this way, only stopping when some needed reactant was consumed or limited in supply by the relative slowness of another reaction. Eventually one or more mineral reactants involved in the two lower temperature reactions would be totally consumed, and one or other of the higher temperature reactions would become the only possible buffer. Further addition of heat would then cause progress of this reaction, elevation of temperature, and continued buffering as long as the mineral reactants remained. In the near-equilibrium or non-equilibrium situation described above, it is possible to calculate the proportions of every phase during the entire process of adding heat to an isobarically invariant assemblage.

In a perfect equilibrium situation, however, it is not possible to determine the relative amounts of heat consumed by the different reactions at the invariant point, because kinetic considerations are not a part of classical equilibrium thermodynamics. However, the linear dependence between the reactions permits a solution to the problem. It will be noticed that reaction R6 is exactly equal to the sum of reactions R3 and R4. Thus, *under conditions of equilibrium* at the invariant point, progress of R3 and R4 together is exactly equivalent to progress of R6 alone. Therefore, after having arrived at the invariant point, production of serpentine by R3 is exactly matched by consumption of serpentine by R4 ,and this combined process is exactly equivalent to simple progress of R6. This leaves the serpentine produced during the buffering by R3 to be destroyed by reaction R5. We can, therefore, regard the process at invariant point FMTS as one in which serpentine is destroyed by R5 and talc plus magnesite is destroyed by R6. The combination of these two reactions must be such as to produce a fluid of invariant composition, and these proportions can be deduced as follows.

For two reactions, indexed "j" and "k", involving ν_{1k} moles of component 1 in reaction "k" and so forth, the number of moles of components 1, n_1, produced will be

$$n_1 = \nu_{1j}y_j + \nu_{1k}y_k$$

where y_j is the amount of reaction "j" that occurs and so forth. Similarly for component 2,

$$n_2 = \nu_{2j}y_j + \nu_{2k}y_k$$

Now, as we only need to know the relative amounts of the reactions, we may substitute the ratio m,

$$m = \frac{y_j}{y_k}$$

and find that

$$m_{jk} = \frac{y_j}{y_k} = -\frac{\nu_{2k} - x_2(\nu_{1k} + \nu_{2k})}{\nu_{2j} - x_2(\nu_{1j} + \nu_{2j})} \tag{5}$$

For reactions R5 and R6 at invariant point [FMTS], equation 5 gives

$$y_{R5} = 3.32\ y_{R6},\ y_{R5} = 0.003,\ y_{R6} = 9.037(10^{-4})$$

Consequently, the destruction of 0.015 moles of S by reaction R5, producing 0.006 moles T and 0.036 moles F, is accompanied by the production by R6 of 0.0036 moles F and destruction of $9.03(10^{-4})$ moles T. The net result is destruction of 0.015 moles S, 0.0045 moles M, and production of 0.0396 moles F and 0.0051 moles T. Converting to grams, these are plotted in figure 7. On the assumption that T was not consumed by R3 enroute to FMTS, then S produced by R3 is the limiting factor. When this S is gone, as calculated above and shown in figure 7,

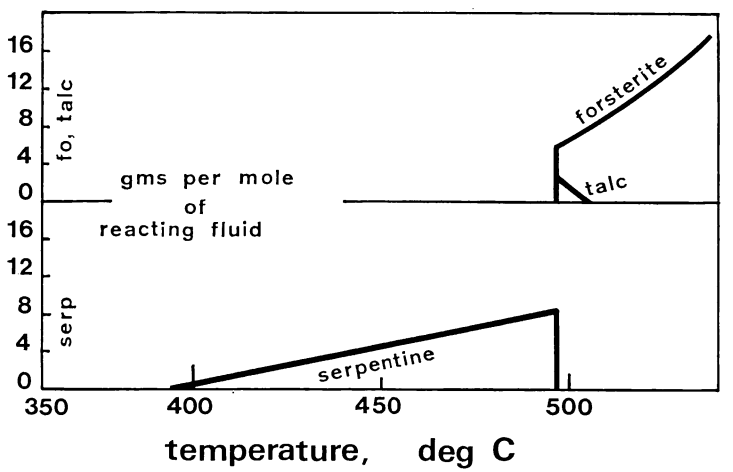

Fig. 7. Variation in abundance of serpentine, forsterite, and talc with increasing temperature in a system with the fluid composition buffered by $T + 3M + 3H_2O = S + 3CO_2$ to the invariant point [FSTM] at 497°C, $x_{CO_2} = 0.076$, followed by reaction at the invariant point destroying the serpentine. Abrupt appearance of forsterite plus talc at the invariant point is accompanied by the abrupt disappearance of serpentine. Weights of phases given with reference to one mole of initial fluid. Smaller amounts of fluid produce proportionately smaller amounts of products.

the assemblage is reduced to M + T + F, and buffering continues along R6, with progressive destruction of T. In this example the 0.0051 moles T produced at FMTS will be finally consumed by R6 at the point where $x_{CO_2} = 0.0985$ on curve R6 (eq 2), which lies at a temperature of 505°C. Beyond this temperature, buffering by R6 can only continue if there is talc in excess of that produced at FMTS.

In figure 7 it can be seen that for a rock to develop 8 g of serpentine by reaction R3 would require interaction with 1 mole (about 18 g) of fluid. At a level of about 10 wt percent fluid, this corresponds to 180 g of rock containing 8 g of serpentine (4% percent), a small but detectable amount. Buffering to [FMTS] thus seems likely for reasonable amounts of fluid, with a smooth increase in the amount of serpentine along the way, finally becoming petrographically detectable. At [FMTS] an abrupt change occurs, with the total destruction of serpentine and the abrupt appearance of forsterite plus talc with the simpler [BMP] example; this discontinuous change would be a good isograd, in contrast to the individual isobaric univariant equilibria, which would not, both because they result in gradual changes in the mineral assemblage and because they do not represent a definite temperature at each pressure.

A similar example may be made of the appearance of tremolite in siliceous marbles. Consider figure 8 (after Skippen, 1971) illustrating the reactions around invariant point 1, involving the phases talc (T), calcite (Cc), dolomite (Dol), tremolite (Tr), quartz (Q), and fluid. Following the same line of argument as in the previous examples, start with one mole of fluid having $x_{CO_2} = 0.2$ at 395°C and a solid phase assem-

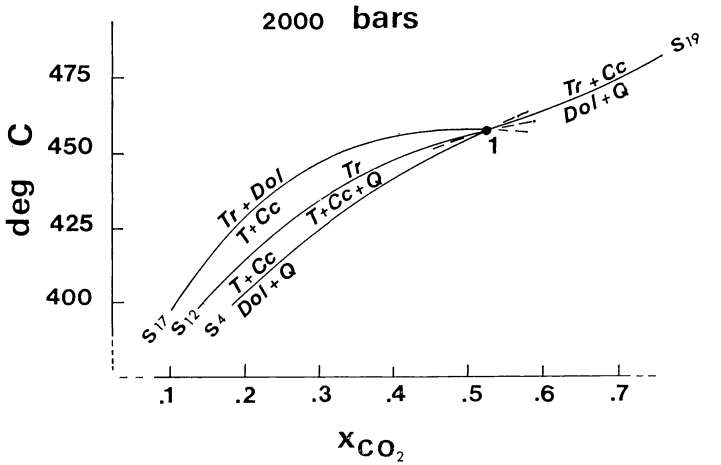

Fig. 8. Isobaric univariant equilibria around the invariant point Dol, Q, T, Cc, Tr at 2000 bars after Skippen (1971). Reactions numbered as in table 10 of Skippen (1971).

blage of Dol + Q. With the addition of heat reaction 4 of Skippen (1971) will be encountered.

$$3\text{Dol} + 4\text{Q} + \text{H}_2\text{O} = \text{T} + 3\text{Cc} + 3\text{CO}_2 \qquad \text{(S4)}$$

Continuous reaction of solids and fluids enroute to the invariant point gives a net increase (compare eq 4) of 0.500 moles CO_2, a net decrease of 0.167 moles of H_2O, and production of 0.167 moles (63.2 g) of talc per mole of initial fluid. This is illustrated in figure 9. Note that the

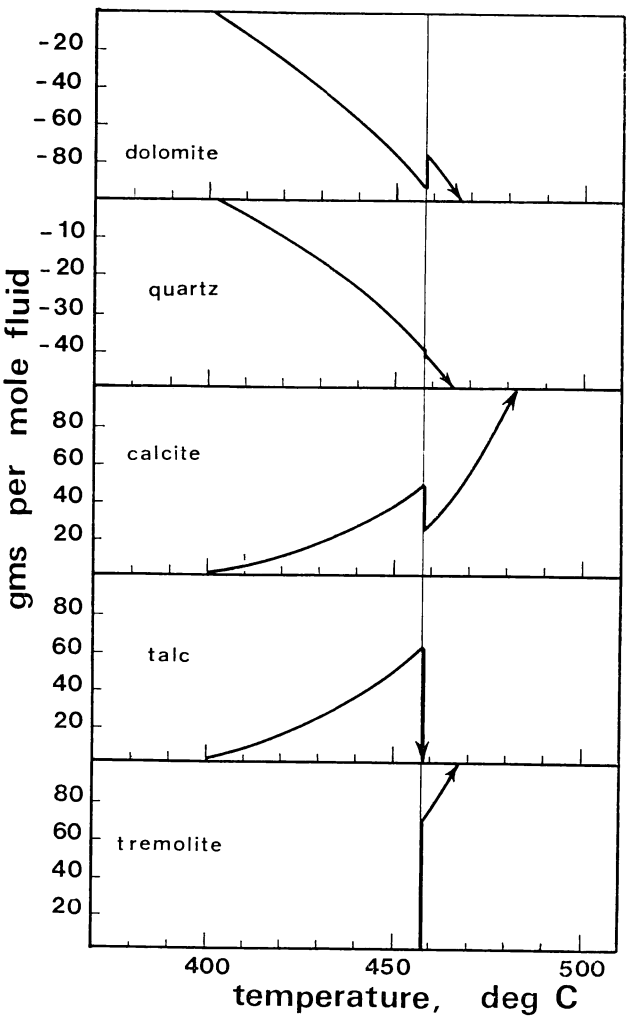

Fig. 9. Variations in abundances of dolomite, quartz, calcite, talc, tremolite with temperature in a CO_2–H_2O fluid buffered by reaction S4 below the invariant point, reactions S17 and S19 at the invariant point, and S19 above. Initial conditions: 1 mole fluid at $x_{CO_2} = 0.20$. Ordinate is grams of mineral per mole of initial fluid. See text for discussion.

growth of talc is non-linear due to the stoichiometry of the reaction. The amount of reaction here is appreciable due to the central location of the starting composition of the fluid and of the invariant point and would certainly be petrographically detectable. It seems likely that in rocks the fluid would be buffered in this way and that below the invariant point the assemblage would be observed to be isobarically univariant but not isobarically divariant as one would expect if x_{CO_2} and T were independent variables. Rocks in and near veins, however, would be expected to be buffered by the fluid and should be isobarically divariant, as determined by counting the number of minerals.

At the invariant point we may consider the simultaneous operation of reactions 17 and 19 of Skippen (1971) in the same way as was done previously for R5 and R6 at FMTS.

$$2T + 3Cc = Tr + Dol + H_2O + CO_2 \qquad (S17)$$

$$8Q + 5Dol + H_2O = Tr + 3Cc + 7CO_2 \qquad (S19)$$

At equilibrium these must operate in the proportions (S17)/(S19) = 77, from equation 5, taking the invariant fluid to have $X_{CO_2} = 0.525$. This proportion is required by the proximity of the invariant point to the temperature-maximum of reaction (S17), which lies at $x_{CO_2} = 0.5$. Reference to figure 3 will show the very low buffering capacity under such conditions, requiring a large extent of reaction to exert an influence on the fluid composition.

The proportions of phases developed during this process are illustrated in figure 9, showing grams of each mineral per mole of initial fluid *versus* temperature. Starting out with dolomite plus quartz and one mole of fluid having $x_{CO_2} = 0.2$, equilibrium buffering of the fluid by reaction S4 results in the following changes. First, dolomite and quartz both decrease in amount. Upon arrival at the invariant point, 0.5 moles (92.2 g) of dolomite and 0.666 moles (40.0 g) of quartz have been consumed by interaction with the initial mole of fluid. At the same time, 0.167 moles (63.2 g) of talc and 0.50 moles (50.0 g) of calcite have been produced. These amounts of phases will be distributed over whatever volume of rock with which the one mole of fluid has reacted. It may seem that the buffering capacity of reaction S4 would soon be exhausted in nature, but it may be worth noting that in a rock consisting entirely of dolomite and quartz in the correct proportions a cube of rock about 4 cm on each side would be able to buffer 23.2 g of fluid with $x_{CO_2} = 0.2$, all the way to the invariant point without running out of either dolomite or quartz. Locally such exhaustion will certainly occur, but it seems likely to the writer that in general the rock should easily be able to cope with the buffering of the fluid phase.

At the invariant point, progress of reaction S17 produces a small increase (0.0833 moles) of dolomite and a still smaller decrease (0.0054 moles) of dolomite by reaction S19, for a net increase of 0.0779 moles (14.4 g) of dolomite. Similarly, quartz is reduced by 0.00866 moles. Tremolite is produced by reaction S17 (0.08333 moles) and by reaction

S19 (0.00108 moles) for a total production at the invariant point of 0.0844 moles (68.6 g). Further addition of heat to the system results in buffering along curve S19 for as long as both dolomite and quartz last.

The petrographically significant features of figure 9 are the abrupt disappearance of talc and the equally abrupt appearance of tremolite. The small increase of dolomite and decrease of calcite at the invariant point would be difficult to observe in rocks. It seems likely that the buffering capacity of the rock might be exhausted somewhere along curve S19, with final occurrence of an isobarically divariant assemblage. Again, smooth change of mineral proportions characterizes the buffering along isobaric univariant curves, and discontinuous changes characterize the passage through invariant points.

Examples from systems involving oxidation-reduction.—Oxidation-reduction equilibria are commonly presented in terms of $\log_{10} f_{O_2}$ versus T diagrams primarily because of the simple connections with thermodynamic theory and with experimental technique. As with carbonate equilibria, one must be wary of assuming that just because these variables are graphically separable they are also petrologically separable. Arguments like those already given indicate that the iron-bearing minerals are frequently excellent buffers of the fluid phase.

First it is appropriate to change variables from the fugacity of oxygen, which is quantitatively insignificant in metamorphic fluids, to the ratio or mole fraction of H_2 in H_2O–H_2 mixtures. This change of variable is possible because of the coupling of f_{H_2}, f_{H_2O}, and f_{O_2} through the reaction

$$H_2O = H_2 + 1/2\ O_2.$$

The stability data on the iron mica annite (Eugster and Wones, 1962) can be represented then in an isobaric T-x_{H_2} diagram. Figure 10 is such a diagram. This shows all the same information as the isobaric log f_{O_2}-T figure of Eugster and Wones and in addition the proportions of the principal constituents of the gas phase, H_2 and H_2O. The advantage of figure 10 for the present problem is that it emphasizes major constituents of the gas phase rather than minor ones, for it is the major ones that are most influential during buffering. Examination of figure 10 will show that as most rocks fall within the stability field of magnetite we can, with advantage, use a larger scale. This change of scale is given in figure 11.

With the help of figure 11, we will consider first reactions involving the pure iron mica, annite, in a binary H_2–H_2O fluid phase. Solid solutions are considered later. Note should be taken of the scale of the fluid composition axis, which shows that all these equilibria are possible only in very H_2O-rich fluids. The reaction

$$\text{Annite} = \text{sanidine} + \text{magnetite} + H_2$$

will, by equation 4, buffer 1 mole of initially pure H_2O to invariant point D (705°C, $x_{H_2} = 0.00155$) with an evolution of 0.00155 moles of

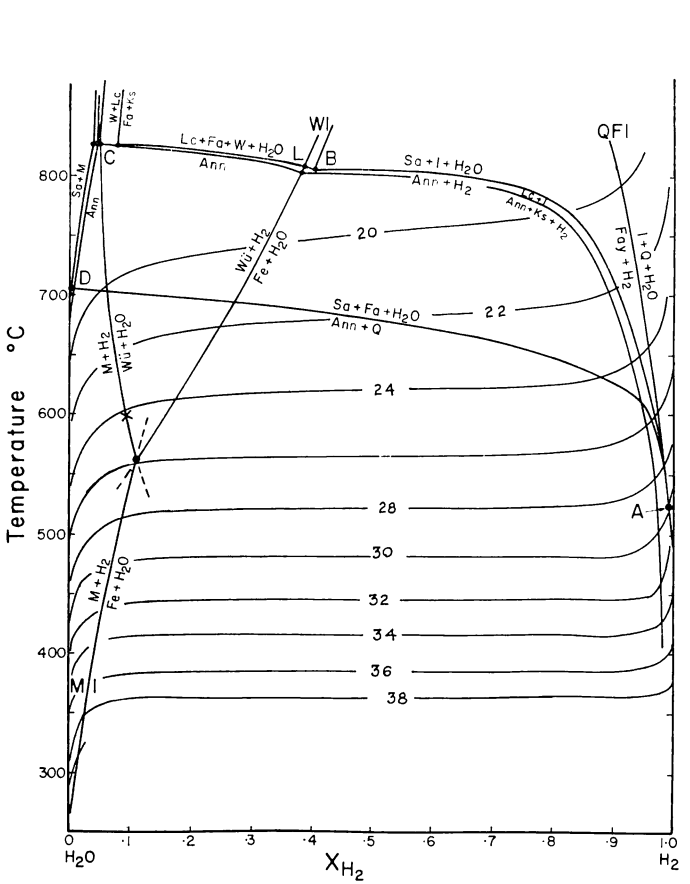

Fig. 10. The stability of the iron mica annite in terms of temperature and mole fraction H_2 (x_{H_2}) in a binary mixture of H_2 and H_2O. Calculated from the data of Eugster and Wones (1962) of the equilibrium relations. The following sources of data were also used: Wagman and others (1945) for the decomposition of H_2O; Shaw (1967) for the mixing properties of H_2–H_2O; Presnall (1969) for the properties of pure H_2; Burnham, Holloway, and Davis (1969) for the thermodynamic properties of H_2O. Invariant points are labelled to correspond to those in figure 7 of Eugster and Wones (1962). Crowding prevents resolution of the details of the several points in the neighborhood of points B, C, and D. Contours of oxygen activity as $\log_{10} f_{O_2}$.

H_2 or to invariant point C (fig. 9) with the evolution of 0.0395 moles of H_2. In either case the reaction products would be petrographically undetectable even though the fluid is continuously buffered. Suppose we begin with annite plus quartz in one mole of essentially pure H_2O. Elevation of the temperature to 705°C would produce 0.00155 moles of K-feldspar per mole of fluid. At the invariant point, cooperation of this reaction with the reaction

$$2 \text{ annite} + 3 \text{ quartz} = 3 \text{ fayalite} + 2 \text{ sanidine} + 2\ H_2O$$

will produce, at equilibrium, a fluid with $x_{H_2} = 0.00155$. This requires, by equation 5, 300 times as much reaction by this second equilibrium as by the first. Consequently abrupt disappearance of either or both of annite and quartz together with the abrupt appearance of sanidine will take place at the invariant point. If quartz is the phase consumed, buffering continues along the curve leading to an invariant point near C (fig. 9), and if annite is consumed, along the QFM buffer curve. Provided we start with a fluid on the H_2O side of the invariant point it seems unavoidable that the minerals will drive the composition of the fluid toward the invariant point with the production of a trivial amount of breakdown products. If there is more H_2 in the fluid than at the invariant point then annite plus quartz will react by the second reaction,

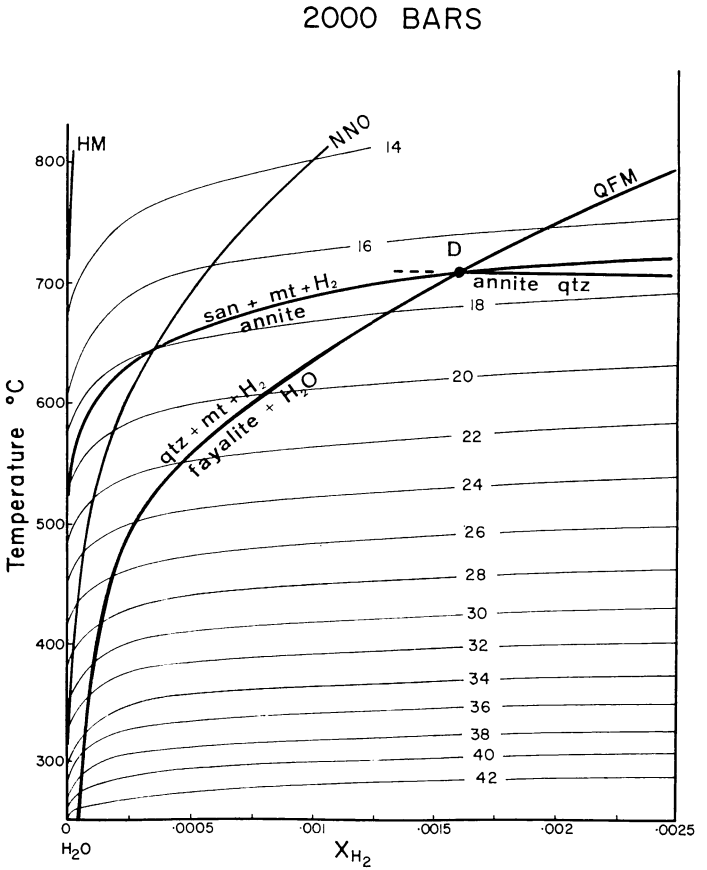

Fig. 11. Stability of the iron mica annite after Eugster and Wones (1962), calculated as in figure 9. Note the very H_2O rich fluid compositions from the small numbers on the x_{H_2} axis.

which will have a very low buffering capacity (see fig. 2, mirror image.) Hence the composition of the fluid may not reach point D from this side.

We should now consider, qualitatively, the role of solid solution, as annite only occurs in nature as one component of biotite. Solid solution of annite with phlogopite will enhance the stability of the iron mica. For example, the curve

$$\text{Annite} = \text{sanidine} + \text{magnetite} + H_2$$

will be displaced to higher temperatures. If we heat such a mica until that displaced curve is intersected, reaction will occur producing K-feldspar plus magnetite and reducing the Fe-content of the biotite. However, as shown above, the extent of reaction enroute to point D is so small that the amount of reaction products would be undetectable and so, therefore, would the change in the composition of the mica. Thus an intermediate biotite will easily drive the composition of the fluid toward a point such as D, displaced according to the composition of the biotite. At such a point, annite component of the biotite will react with quartz, making the biotite now much more Mg-rich and producing a definite change in mineral proportions. Even under these conditions of sliding equilibrium the fluid will remain buffered by the assemblage but not of course to either a fixed value or to any one of the end-member curves shown in figures 10 and 11.

As a final example, the stability of chloritoid (Ganguly, 1969) can be recalculated into T-x_{H_2} coordinates. The location of one of the invariant points is shown in figure 12, in which the reaction boundaries are only diagrammatic. The important feature to notice in figure 12 is the very low x_{H_2} at the invariant point, making the reactions

$$\text{Chloritoid} + \text{magnetite} + \text{quartz} + 2H_2 = \text{almandine} + 5H_2O$$

and

$$\text{Chloritoid} = \text{staurolite} + \text{magnetite} + \text{quartz} + 38H_2O + 10H_2$$

highly effective buffers. Of these two, the first will be the more effective due to its stoichiometry. Both can easily drive the composition of a water-rich fluid to the invariant point. The reaction

$$\text{Chloritoid} + \text{quartz} = \text{staurolite} + \text{almandine} + H_2O$$

by contrast is a poor buffer under these conditions and thus must be the main reaction forming staurolite and almandine at the expense of chloritoid. It seems clear that it will be very difficult to impose a temperature and f_{O_2} independently on such a rock, and that in general the sequence of reactions observed in rocks containing chloritoid should depend upon initial proportions of the non-volatile constituents and on the amount of fluid involved, rather than on a simple-looking increase of temperature at a constant or externally controlled f_{O_2}.

Accessibility of invariant points along buffer-paths.—A consequence of progressive buffering of pore fluids along mineral equilibrium boundaries is that ideally the fluids should change in composition from one

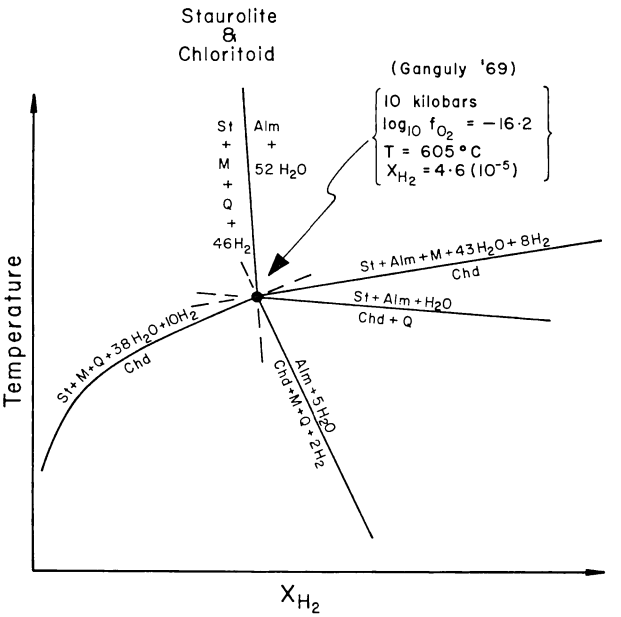

Fig. 12. Diagrammatic stability of chloritoid in terms of temperature and x_{H_2} at 10 kb. Composition of the isobarically invariant fluid calculated assuming ideal mixing of H_2 and H_2O. Locations of reaction curves are diagrammatic only.

invariant point to the next, the route followed depending on the proportions of the non-volatile components. However, it is not possible by this method to get from any one invariant point to every other one, the possibilities being limited by the inter-connections along the isobaric univariant curves. This is illustrated in figure 13 for the system MgO–SiO_2–H_2O–CO_2.

The lower part of figure 13 shows diagrammatically the isobaric T-x_{CO_2} relations, and the upper part the interconnections between the invariant points consistent with this topology of the diagram. It is important to note that as the observable discontinuous changes in assemblages occur at the isobaric invariant points, then the polybaric P-T projections of these invariant points must be regarded as the main candidates for isograds in rock falling within this system and not the isobaric univariant curves. Accordingly, figure 13 shows, in the upper part, the polybaric univariant conditions consistent with the experimental work of Johannes (1969), Walter, Wyllie, and Tuttle (1962), and Greenwood (1967). It should be noted that these are not univariant reactions, but conditions, as the exact reaction that gives the change in mineralogy at each curve depends on the bulk composition.

Figure 13 illustrates the solution to the difficulty noted in the early part of this paper. That is, that petrologically we seem able to make consistent sense out of the order of appearance of phases, while the com-

plexity of T-x diagrams would suggest a much wider range of sequences than we observe. The problem is much diminished, if buffering of the fluid by the minerals is effective.

Figures 14 and 15, respectively, give the univariant equilibrium conditions for the iron mica, annite (Eugster and Wones, 1962) and chloritoid (Ganguly, 1969). For reasons already explained, these are regarded as the main boundaries at which phase assemblages undergo discontinuous changes in biotite- and chloritoid-bearing rocks.

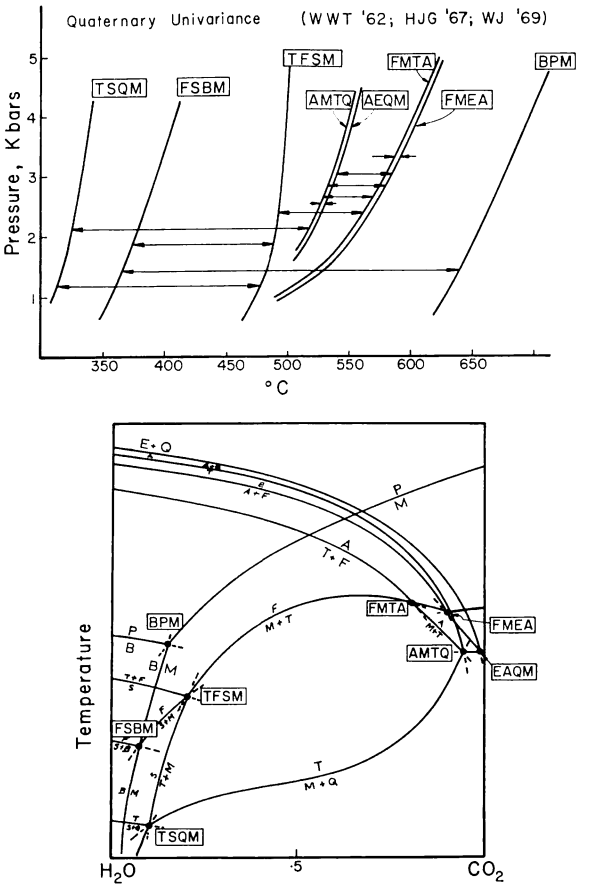

Fig. 13. Bottom. Diagrammatic T-x section for the system MgO–SiO_2–H_2O–CO_2 after Johannes (1969) and Greenwood (1967). Top. Polybaric univariant curves corresponding to the isobaric invariant points shown in the bottom part of the diagram. Position of the curves form the experimental work of Walter, Wyllie, and Tuttle (1962), Greenwood (1967), and Johannes (1969). The univariant P-T curves are not all accessible from one another by way of isobaric univariant buffer curves. The connections that are possible are shown in the upper part of the figure by arrows.

SUMMARY AND CONCLUSIONS

It is proposed that in many progressively metamorphosed rocks, particularly those metamorphosed in the presence of a 2-component fluid phase such as H_2O–CO_2 or H_2–H_2O, the mineral equilibria are capable of buffering the composition of the fluid phase unless it is present in a very large amount. One of the consequences is that the abrupt appearance of new minerals is most likely to coincide with isobaric invariant points rather than with isobaric univariant equilibria. Separability of variables such as f_{O_2}, f_{H_2}, x_{CO_2}, temperature, and pressure may not therefore always coincide with petrologic reality, and experimental and theoretical diagrams emphasizing such separation of variables should always be examined to see if buffering processes may operate.

This view is not inconsistent with the recent study by Nokleberg (1973), as he drew particular attention to the oxidation-reduction processes that occur upon addition of CO_2 to a mixture of H_2 and H_2O in proportions consistent with the upper stability of graphite. He shows that under these conditions the buffering capacity of metasomatized rocks will be exceeded soon, as would be predicted with the present study under such conditions, where the reacting gas species are all present in significant proportions in the fluid phase.

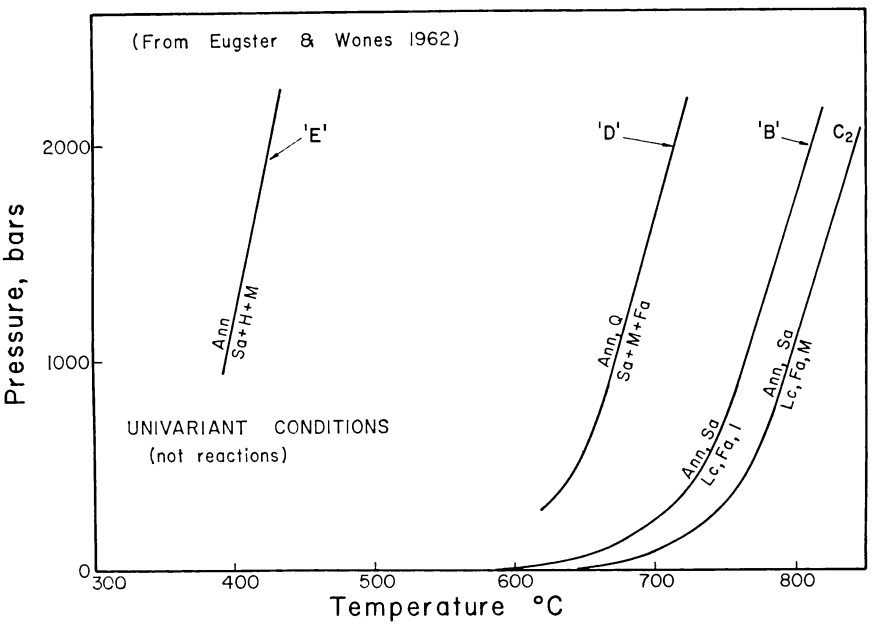

Fig. 14. Polybaric univariant curves involved in the stability of the iron mica, annite (Eugster and Wones, 1962). These are the boundaries to which the fluid compositions will be driven by the buffering process in H_2–H_2O mixtures and which will provide the only observable discontinuous reaction in the end-member assemblages.

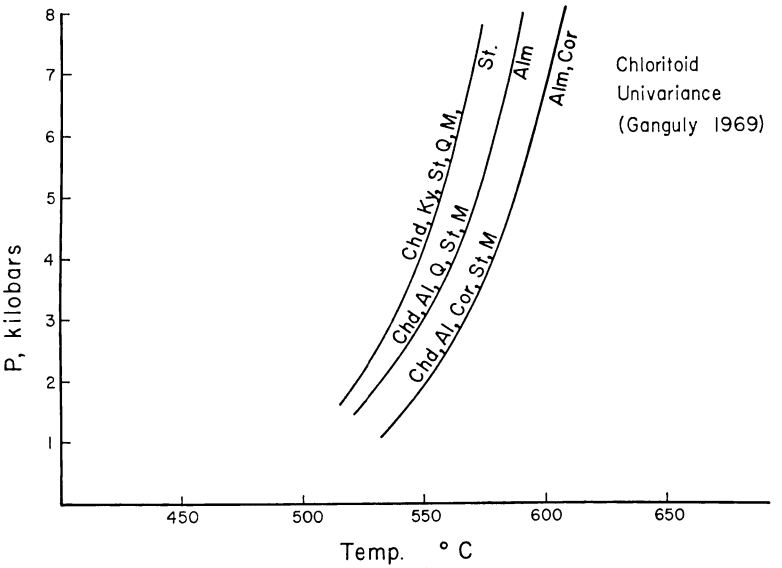

Fig. 15. Polybaric univariant curves involved in the stability of chloritoid. (Ganguly, 1969). It should be noted that the univariant P-T curves of figures 12, 13, and 14 are not labelled "univariant reactions". This is because the exact reaction that occurs at the curve will depend in each case on the proportions of non-volatile constituents. At any curve all of the reactions will take place at the same temperature due to having been buffered over to the isobaric invariant point.

A recent contribution by Trommsdorff (1972) provides independent evidence that the buffering process is important in siliceous carbonate rocks. In particular, he draws attention to the equilibrium illustrated here in figure 8, involving quartz, dolomite, calcite, talc, tremolite, and fluid. It is interesting that buffering seems to have operated in these rocks, particularly as, according to equation 4 and figures 1 through 4, these should be the most difficult to buffer. One must conclude that if the minerals of these rocks can buffer the metamorphic fluid, then surely most rocks must be self-buffering. If buffering is assumed to have occurred then the mineral proportions in progressively metamorphosed rocks should be adequate to estimate the amount of fluid that has passed through a given volume of rock in at least a semi-quantitative way.

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