

## Are reversed Fe-Mg exchange and solid solution experiments really reversed?

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### ABSTRACT

Numerous experimental studies investigating Fe-Mg exchange and other solid solution variations in minerals have claimed to have reversed their results because of apparent convergence to the equilibrium composition from opposing compositional directions. These reversals are actually apparent compositional brackets that, in many cases, cannot be reversed. Furthermore, it is likely that many if not all apparent compositional brackets are not strictly limiting, in the sense that they may not unequivocally constrain a compositional interval within which the equilibrium composition must lie. A true compositional bracket is obtained most confidently if a single compositional parameter (e.g., Fe-Mg exchange) is isolated and a continuous diffusional controlled compositional gradient from the starting to the final composition is established. The gradient indicates the direction of the equilibrium composition required by the concept of bracketing. In contrast, an equilibration mechanism involving multicomponent solution and precipitation typically involves variation in several rather than one compositional parameter and may result in compositional discontinuities between initial and final compositions, opening the possibility of jumping to metastable compositions. In such situations, the identification of the direction to equilibrium from the final compositions becomes ambiguous, and the logical basis for bracketing is lost. Analysis of the large, apparently reversed experimental data set of Pattison and Newton (1989) on garnet + clinopyroxene Fe-Mg exchange shows first that the experiments were not truly reversed and second that the equilibration mechanism was mainly multicomponent solution and precipitation with negligible diffusion, with the result that the experiments were not unequivocally bracketed. Examination of several other Fe-Mg exchange and solid solution experimental studies suggests a similar conclusion. Calculated diffusion-penetration distances suggest that diffusion should not be expected to cause measurable compositional changes in normal experiment times. Unreversed (and in many cases probably not strictly bracketed) solid solution experiments using crystalline starting materials yield consistent compositional trends as a function of pressure, temperature, and other intensive parameters, which are necessary, if not sufficient, indications that equilibrium was closely approached. The lack of true reversals nevertheless influences the way in which thermodynamic data are extracted from such experiments.

### INTRODUCTION

Reversibility is regarded as an essential demonstration that equilibrium has been attained in phase equilibrium experiments (Holloway and Wood, 1988, p. 11). Unreversed or unbracketed experiments are open to criticism because of the possibilities that equilibrium compositions were not attained or that the phase assemblage or phase compositions were misinterpreted.

Several studies have calibrated Fe-Mg exchange thermometers on the basis of what are claimed to be reversed experiments using crystalline starting materials (e.g., garnet + biotite: Ferry and Spear, 1978; garnet + clinopyroxene: Pattison and Newton, 1989; garnet + olivine: Hackler and Wood, 1989; garnet + orthopyroxene: Eckert and Bohlen, 1992; clinopyroxene + olivine: Perkins and Vielzeuf, 1992). Many other experimental studies also have claimed to have reversed compositions of solid so-

lution minerals in various assemblages for purposes of geothermometry, geobarometry, and determining activity-composition relations (e.g., diopside-enstatite solid solutions: Lindsley and Dixon, 1976; Nickel et al., 1985; Al solubility of pyroxenes in equilibrium with garnet: Perkins and Newton, 1980; Lane and Ganguly, 1980; Perkins et al., 1981; Ca in olivine in equilibrium with clinopyroxene: Adams and Bishop, 1986; calcium-iron-magnesium-manganese garnet compositions in a variety of assemblages: Koziol and Newton, 1989; Koziol, 1990; Koziol and Bohlen, 1992). In all these experimental studies, crystalline starting materials were used to avoid the potential problems of nucleation and the persistence of metastable crystalline compositions from disordered, high free-energy starting materials such as glass or gels. The other theoretical advantage is that changes in the compositions of crystalline starting materials might be used

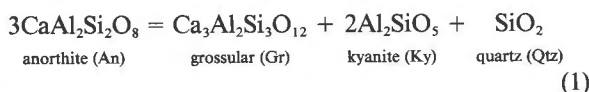
to indicate the direction to equilibrium, even if equilibrium compositions themselves were not attained.

The purpose of this study is to evaluate whether solid solution experiments using crystalline starting materials provide either reversals or limiting brackets of equilibrium compositions. First, a distinction is made between a reversal and a compositional bracket: I argue that what are referred to as solid solution reversals are actually apparent compositional brackets that, in many cases, cannot be reversed. Second, I argue that a true compositional bracket, defining a compositional interval within which one is certain the equilibrium composition must lie, can only be obtained confidently if the phases equilibrated by a diffusively controlled mechanism rather than by a multicomponent solution and precipitation mechanism, the latter of which introduces several theoretical and analytical complications. Several published experimental studies, including Pattison and Newton's (1989) apparently reversed study on the Fe-Mg exchange between clinopyroxene and garnet, are examined to evaluate reaction mechanisms and the extent to which the experimental results were either reversed or unequivocally bracketed. Experimental diffusion data are used to calculate the diffusion penetration distances for typical experiment times to see whether diffusional exchange by itself is fast enough to allow significant compositional change. Although the results of these investigations suggest that most solid solution experiments involving crystalline starting materials equilibrate by a multicomponent solution and precipitation mechanism and consequently do not provide either true reversals or unequivocal brackets of equilibrium compositions, several lines of evidence suggest that the experimental results represent a close approach to equilibrium and are superior to synthesis experiments using glass or gel starting materials. Nevertheless, these considerations carry implications for the techniques used to extract thermodynamic data from such experiments.

## REVERSAL VS. COMPOSITIONAL BRACKETING EXPERIMENTS

### Reversal experiments

Reversibility and equilibrium bracketing are commonly taken to be synonymous, even though there are subtle differences between the two. A general definition of reversibility is the ability to reverse the direction of a reaction by changing  $P$ ,  $T$ , or the composition of the system (Holloway and Wood, 1988, p. 11). This is most easily understood in the context of a univariant reaction involving phases of fixed composition such as



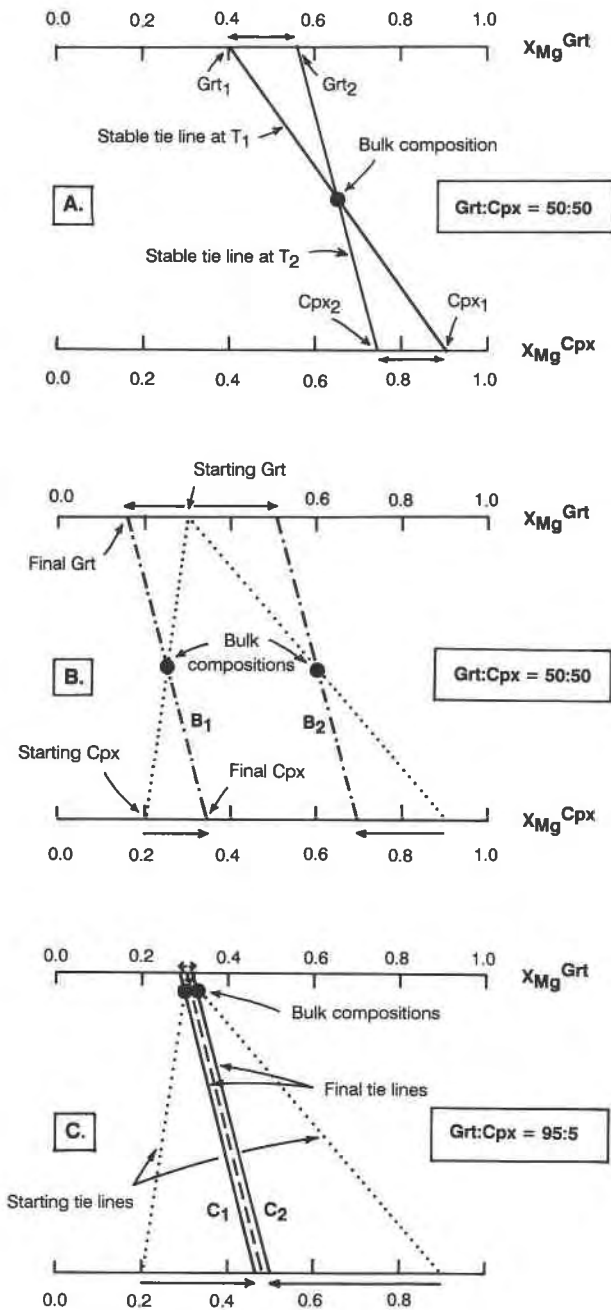
(1)

in the system  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$  (e.g., Koziol and Newton, 1988). The equilibrium compositions of the minerals in the mineral assemblage are known in advance (stoichiometric end-members) and do not change significantly over

the  $P$ - $T$  range of the experiments, so they can be synthesized individually in advance and added together to make mineral mixes. An experimental reversal between phase assemblages A (An) and B (Gr + Ky + Qtz) involves two experiments at different  $P$ - $T$  conditions containing a mixture of the two phase assemblages (i.e., An + Gr + Ky + Qtz). At one  $P$ - $T$  condition, phase assemblage A (An) grows at the expense of phase assemblage B (Gr + Ky + Qtz), from which one can conclude that the free energy,  $G$ , of assemblage A is less than that of assemblage B, i.e.,  $G_{\text{An}} < G_{\text{Gr+Ky+Qtz}}$  (Gordon, 1973). At the second  $P$ - $T$  condition, phase assemblage B (Gr + Ky + Qtz) grows at the expense of phase assemblage A (An), from which one can conclude that  $G_{\text{Gr+Ky+Qtz}} < G_{\text{An}}$ . In both cases, the driving force for the reaction is the minimization of the total free energy of the system. The equilibrium  $P$ - $T$  condition for the univariant equilibrium, at which  $G_{\text{An}} = G_{\text{Gr+Ky+Qtz}}$ , must lie between these two  $P$ - $T$  conditions, thereby establishing the concept of equilibrium bracketing. The sense of reversal comes from phase assemblage A (An) forming from phase assemblage B (Gr + Ky + Qtz) at the first  $P$ - $T$  condition and vice versa at the second  $P$ - $T$  condition, such that the two assemblages are alternately products and reactants for each other (if one assumes that no metastable intermediate reaction products formed).

In experiments involving phases whose compositions can vary (i.e., show solid solution), reversibility and equilibrium bracketing may not be equivalent. Taking Fe-Mg exchange between garnet and clinopyroxene as an example, a theoretical reversal of their Fe-Mg ratios might involve a pair of experiments such as illustrated in Figure 1A, with the assumptions that only Fe and Mg are exchanging, that Fe-Mg diffusion is fast enough in the two minerals that the reacting bulk composition is the same as the inserted bulk composition, and that there are no kinetic barriers to the attainment of equilibrium. At temperature  $T_1$ , garnet and clinopyroxene are assumed to have the equilibrium compositions  $\text{Grt}_1$  and  $\text{Cpx}_1$ . When temperature is changed from  $T_1$  to  $T_2$ , the total free energy of the system,  $G$ , is lowered by the Fe-Mg ratios of  $\text{Grt}_1$  and  $\text{Cpx}_1$  changing to those of  $\text{Grt}_2$  and  $\text{Cpx}_2$ , such that  $G_{(\text{Grt}_2+\text{Cpx}_2)} < G_{(\text{Grt}_1+\text{Cpx}_1)}$ . If temperature changes from  $T_2$  back to  $T_1$ , then  $\text{Grt}_2$  and  $\text{Cpx}_2$  change in Fe-Mg ratio back to  $\text{Grt}_1$  and  $\text{Cpx}_1$ , such that at  $T_1$ ,  $G_{(\text{Grt}_1+\text{Cpx}_1)} < G_{(\text{Grt}_2+\text{Cpx}_2)}$ .

Although the above theoretical example satisfies the requirements of a reversal in the sense that the direction of the reaction is reversed and that each phase assemblage is alternately a reactant or product for the other, there are several problems in its practical implementation. One is that starting materials comprising coexisting mineral compositions in chemical equilibrium at  $T_1$  must somehow be synthesized. Otherwise,  $\text{Grt}_2$  and  $\text{Cpx}_2$  would be unlikely to change in composition back to  $\text{Grt}_1$  and  $\text{Cpx}_1$  when the temperature was changed from  $T_2$  to  $T_1$ , and the criterion of reversibility would be lost. However, because this information cannot be known a priori, the above



theoretical experiment would be very difficult to create in practice. One possibility might be to use as starting materials coexisting minerals crystallized in synthesis experiments and to employ an iterative approach involving several experiments such as described above until the minerals repetitively change to the same compositions, going back and forth from  $T_1$  to  $T_2$ .

Even if the first problem were overcome, there are two more problems common to all solid solution experiments: (1) how can one be sure that the phases in fact change to the equilibrium (most stable) compositions rather than to more stable, but possibly metastable, com-

positions and (2) even if the phases do change to equilibrium compositions, how can one be sure that the equilibrated portions are correctly identified and measured?

Fig. 1. Schematic representation of tie-line rotations involving  $X_{Mg}$  [= Mg/(Mg + Fe)] of garnet and clinopyroxene, if one assumes infinitely fast diffusion. Labeled tie lines correspond to labeled points in Fig. 2. (A) Stable tie lines for two temperatures. (B) Initial and final tie lines for two pairs of garnet and clinopyroxene in equal modal abundance at one temperature. Dotted lines represent tie lines connecting compositions that are initially out of equilibrium. Dash-dot lines are tie lines connecting final equilibrium compositions. Arrows show direction of compositional change of garnet and clinopyroxene going from initial to final compositions. (C) Garnet present in overwhelming abundance relative to clinopyroxene. Solid lines are tie lines connecting equilibrium compositions. The dashed line represents a tie line connecting equilibrium compositions given no change in garnet composition during the experiment. Other symbols are the same as in B.

### Compositional bracketing experiments

The solution has been to use an apparent convergence technique, popularly known as a compositional reversal, which uses the principle of bracketing equilibrium compositions from opposing compositional directions (e.g., Ferry and Spear, 1978; Pattison and Newton, 1989; Kozioł and Newton, 1989). The approach, although straightforward in theory, is difficult in practice. First, as pointed out by Perkins and Newton (1980) and others, it is necessary to isolate the variation in a single compositional parameter or exchange vector (e.g., Fe-Mg exchange), which may be difficult in phases that can vary in several compositional parameters. If more than one compositional parameter varies in the experiment, one cannot be sure to what extent the variation in the desired compositional parameter is controlled by variation in the other parameters.

Second, achieving a convergence requires a special experimental design. Again taking Fe-Mg exchange between garnet and clinopyroxene as an example, the approach is to allow the Fe-Mg composition of either garnet or clinopyroxene to vary in response to changes in either  $P$  or  $T$  or one other compositional parameter. A convergence in Mg/(Mg + Fe) would be obtained by inserting two clinopyroxenes with Mg/(Mg + Fe) ratios that are out of equilibrium, such that, as the minerals changed compositions to lower the total free energy of the system, the final equilibrium composition would be constrained by the approach from the Fe-rich and Mg-rich directions in the two experiments. Even if the final compositions did not coincide, the equilibrium composition in theory must lie between them, thereby establishing a compositional bracket.

Although it establishes a bracket, such an experiment still might not be a true reversal because it might never

be possible to recreate the starting compositions that are initially out of equilibrium from the final mineral compositions (i.e., reverse the experiment) simply by changing  $P$ ,  $T$ , or one other compositional parameter. For example, recreating a starting garnet + clinopyroxene pair in which garnet is more magnesian than clinopyroxene is impossible because garnet is always less magnesian than coexisting clinopyroxene in nature. For convergence experiments of this kind, the term compositional reversal should be abandoned in favor of compositional bracket.

A third requirement for such an experiment, implicit in the concept of convergence to equilibrium, is that the direction to equilibrium can be demonstrated. This is a substantial problem because sluggish intragranular diffusion rates inhibit the attainment of equilibrium in experiment times (see below).

### ISOLATION OF ONE COMPOSITIONAL PARAMETER

In the above example of Fe-Mg exchange between garnet and clinopyroxene, the isolation of Fe-Mg change in only one of garnet or clinopyroxene is impossible because the Fe-Mg composition of one can change only through exchange with the other. In Figures 1B and 2, if garnet and Fe-rich clinopyroxene are inserted in equal modal abundance into an experiment and equilibrate, Fe-Mg exchange between both phases gives a tie-line rotation in Figure 1B that corresponds to vector  $B_1$  in Figure 2. If the same experiment is repeated with an Mg-rich clinopyroxene, vector  $B_2$  results. The two experiments do not bracket any one point on the equilibrium isotherm (other than in a very loose way) because both the garnet and clinopyroxene changed in Mg/(Mg + Fe) during the experiments, which result in vectors that diverge rather than converge (see Fig. 2). Although each individual vector probably represents an approach to equilibrium, one cannot be sure that a longer experiment time or more analyses of the rim compositions wouldn't produce a different final composition (and hence a change in length or direction of the vector) for one or other of the two minerals.

Ferry and Spear (1978) were the first to propose a method that overcame this problem in their calibration of the garnet + biotite Fe-Mg exchange thermometer. They reasoned that if an overwhelming abundance of one of the exchanging Fe-Mg minerals (garnet) were inserted into the experiments, then, from the mass balance, the other mineral (biotite) could change in composition substantially, with negligible change in the composition of the garnet (see Figs. 1C and 2). In principle, this approach had many advantages: (1) it effectively reduced the number of minerals changing composition in the experiment from two to one, thereby eliminating the need to analyze one of the minerals (garnet) as a potential source of uncertainty; (2) it seemed to provide a kinetic advantage in that the extent of the Fe-Mg exchange of garnet, relatively the more sluggish of the two minerals to participate in Fe-Mg exchange, would be minimized; and (3) it allowed an effective (although not strict) bracketing of the Mg/(Mg + Fe) composition of biotite in equilibrium with a

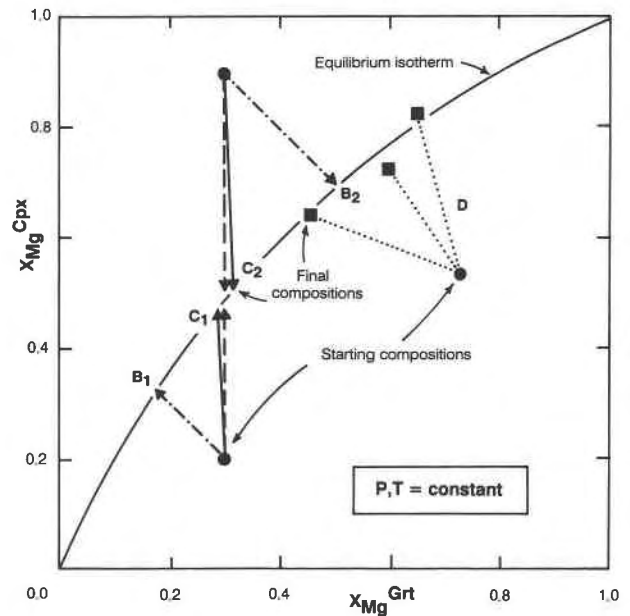


Fig. 2. Schematic Fe/Mg distribution isotherm at constant temperature and pressure. Curve is the equilibrium isotherm. Solid circles represent starting compositions, corresponding to the dotted tie lines in Fig. 1B and 1C. Labeled arrowheads and squares represent final compositions, corresponding to the labeled tie lines in Fig. 1. Solid, dashed, and dash-dot vectors represent the direction of change from initial to final composition, corresponding to tie-line rotations in Fig. 1. Squares are the final compositions for different modal proportions of starting composition  $D$ . Squares and dotted lines rather than arrows are used to show that there may not be a continuous compositional gradient from initial to final compositions (see text).

single garnet by convergence to an intermediate composition from Fe-rich and Mg-rich starting compositions (see tie lines  $C_1$  and  $C_2$  in Fig. 1A and corresponding vectors in Fig. 2). An underlying assumption made by Ferry and Spear was that the only compositional change induced in garnet and biotite in the experiments was Fe-Mg exchange. Pattison and Newton (1989), Hackler and Wood (1989), Eckert and Bohlen (1992), and Perkins and Vielzeuf (1992) applied the same principles in their attempts to bracket Fe-Mg exchange between garnet + clinopyroxene, garnet + olivine, garnet + orthopyroxene, and clinopyroxene + olivine, respectively. This approach appeared to achieve its aim: the exchanging minerals, which were in small modal abundances in pairs of experiments (e.g., biotite in Ferry and Spear; clinopyroxene in Pattison and Newton), afterward had intermediate Fe-Mg compositions that generally agreed quite closely.

In contrast to Fe-Mg exchange experiments, Koziol and Newton's (1989) and Koziol's (1990) experiments on grossular activity-composition relationships in calcium-iron-magnesium garnets were based on the displacement of the equilibrium  $Grs = An + Ky + Qtz$  for garnets of different composition. These experiments involved only

one solid solution phase, garnet, so that apparent brackets of garnet compositions could be obtained without the complications of compositional variations in the other phases.

#### IDENTIFICATION OF THE DIRECTION TO EQUILIBRIUM: REACTION MECHANISMS

##### Diffusion vs. solution and precipitation

An important underlying assumption in the above approach is that starting compositions that were initially out of equilibrium converged to the final equilibrium composition, thereby establishing the direction to equilibrium required by the concept of bracketing. In experiments in which the inserted out-of-equilibrium compositions are preserved in portions of the mineral grains (e.g., clinopyroxene in Pattison and Newton; olivine in Hackler and Wood), evidence for convergence to equilibrium is best provided in theory by a continuous, diffusionally controlled compositional gradient from the unreacted seed composition to the equilibrated rim composition (Figs. 3A and 4A). Each successive spot down the gradient represents a lower free energy (more stable) composition, such that even if the final equilibrium composition is not attained or cannot be measured, the direction to equilibrium is unambiguous (Figs. 3A and 4A). Moreover, as discussed by Goldsmith and Newton (1974, p. 341–343 and their Fig. 1), it is thermodynamically impossible to overstep the equilibrium by this mechanism because this would involve forming a composition with relatively higher free energy at the expense of a composition with lower free energy. Consequently, convergence from the opposing compositional directions establishes an unequivocal bracket of the equilibrium composition.

In contrast, the development of newly formed compositions by recrystallization or solution and precipitation violates the requirement for bracketing of equilibrium, because these mechanisms may result in jumps to compositions that for kinetic reasons may overshoot or undershoot the stable equilibrium composition (see Figs. 3B and 4B). Such a process is thermodynamically permissible in the sense that the new compositions are more stable, i.e., have a lower free energy, than their respective starting compositions, even if they are not the most stable compositions (see the discussion in Goldsmith and Newton, 1974). Several authors have observed this effect in some of their experiments, including Bachinski and Müller (1971) in experiments on the alkali feldspar solvus, Lindsley and Dixon (1976) in experiments on the enstatite-diopside system, Perkins and Newton (1980) in experiments on the Al solubility of orthopyroxene in equilibrium with garnet, and Pattison and Newton (1989) in garnet + clinopyroxene Fe-Mg exchange experiments. The result is apparent compositional overlaps in pairs of experiments starting from opposing compositional directions. In such a situation, there is no guarantee that the

newly formed compositions will subsequently approach equilibrium from the same compositional direction as the starting material (see Fig. 4B). If knowledge of the direction to equilibrium from the final compositions is lost, the basis for establishing an unequivocal bracket of the equilibrium is also lost. For example, in experiments in which compositional overlaps are observed, one cannot be certain whether the equilibrium composition lies within the range of the compositional overlap or outside the range. Even if nonoverlapping apparent brackets from pairs of experiments are obtained, there is no guarantee that the equilibrium composition lies within the range of the apparent bracket (see Fig. 4B).

These considerations indicate that to achieve unequivocal compositional brackets, the equilibration mechanism must be controlled by intragranular diffusion of the elements of interest. In contrast, a multicomponent solution and precipitation mechanism involves the participation of an intermediate phase, typically an intergranular fluid or melt, into which the inserted compositions dissolve and from which new, more stable (but not necessarily equilibrium) compositions precipitate either onto preexisting seed grains or as new crystals (Fig. 4B). This process is unidirectional in the sense that all the starting material will eventually be consumed, given enough time and the absence of kinetic barriers, and that in many cases it will be impossible to remake the starting compositions from the final compositions. Strictly speaking, such experiments are a kind of synthesis experiment, in which the starting materials are crystalline materials rather than glass or gels. Moreover, in experiments involving phases that show solid solution on more than one crystallographic site, a solution and precipitation mechanism usually results in changes in more than one compositional parameter, further eroding the criterion of strict bracketing.

##### The effect of fluid

The presence or absence of a fluid phase has a major effect on experimental reaction rates and reaction mechanisms (Rubie and Thompson, 1985). Fyfe and Verhooogen (1958) estimated that the presence of even small amounts of H<sub>2</sub>O increased reaction rates by 8–10 orders of magnitude, most likely because of solution and precipitation. A compilation of rate constants for dissolution and phase equilibrium experiments in the presence of fluid by Wood and Walther (1983) shows that the average logarithm to the base 10 of the rate constant at 800 °C is about  $-9.5 \text{ cm}^2/\text{s}$ , compared with interdiffusion coefficients for Fe-Mg exchange in garnet and clinopyroxene at 800 °C of  $-15$  to  $-17 \text{ cm}^2/\text{s}$  and for Al diffusion in clinopyroxene at 800 °C of  $-20 \text{ cm}^2/\text{s}$  (see the references listed at the bottom of Table 1). These data support the conclusions of Rubie (1986) and Lüttge and Metz (1993) that, in the presence of H<sub>2</sub>O-bearing fluid, reactions proceed mainly by a solution and precipitation mechanism.

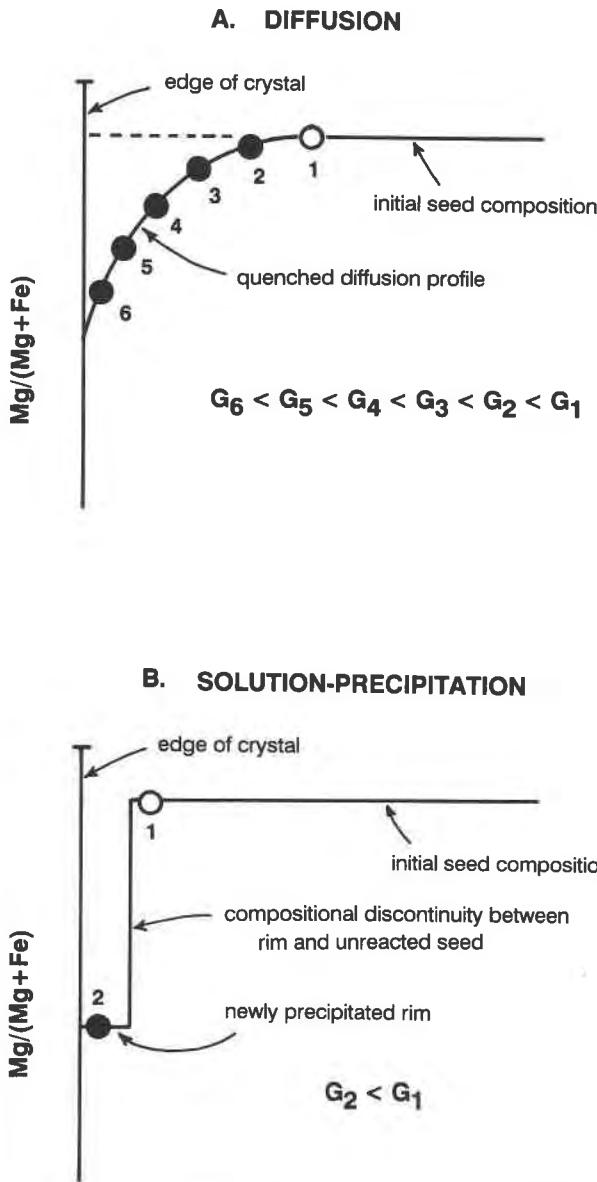


Fig. 3. Schematic illustration of contrasting core-rim compositional profiles arising from diffusion and solution and precipitation equilibration mechanisms. With reference to Fig. 4, the mineral illustrated is clinopyroxene. Numbered circles correspond with those in Fig. 4. (A) Diffusion: the open circle (1) = starting seed composition, solid circles (2-6) = individual points on the quenched diffusion profile. From the starting composition toward the rim, the free energy of each successive quenched point on the profile is lower than the previous one. (B) Solution and precipitation: the open circle (1) = starting seed composition, the solid circle (2) = composition of precipitated rim. An abrupt compositional discontinuity may occur between the precipitated rim and the seed crystal. The free energy of the rim composition, whether stable or metastable, is nevertheless lower than the starting composition.

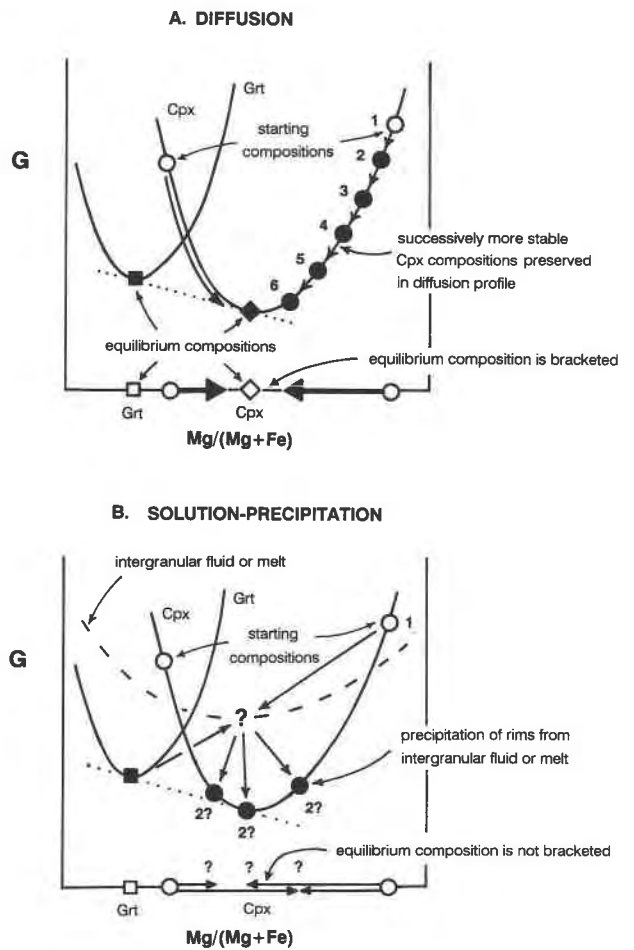


Fig. 4. Schematic free energy ( $G$ ) vs.  $Mg/(Mg + Fe)$  plots, showing contrasts between diffusively controlled and solution and precipitation equilibration mechanisms. Garnet is assumed to be present in overwhelming abundance so that only clinopyroxene shows observable compositional change. Numbers correspond to those in Fig. 3. (A) Diffusion: open circles = two starting clinopyroxene compositions, one more Fe-rich and the other Mg-rich than the equilibrium composition. Numbered solid circles show the lowering of free energy of the clinopyroxene (and hence of the system) as it changes composition going down a diffusional profile from the initial Mg-rich seed material toward the Fe-richer rim. If the Fe-rich starting clinopyroxene develops a complementary Mg-richer rim by diffusion, the two experiments, even if they do not attain the equilibrium composition, nevertheless provide an unequivocal bracket of the equilibrium composition. (B) Solution and precipitation: starting compositions as in A. The equilibration mechanism involves a two-step process (arrows): first, solution of clinopyroxene and garnet into an intergranular fluid or melt (dashed arrow), the composition of which is unknown (?), and second, precipitation of rims or new crystals of clinopyroxene, the compositions of which are of a lower free energy than the starting clinopyroxene, but for kinetic reasons may not necessarily be the equilibrium composition (?). The equilibrium composition cannot therefore be bracketed using the final compositions.

TABLE 1. Calculated diffusion penetration distances in minerals in experiment times

Expt. conditions			Diffusion penetration distance ( $\mu\text{m}$ ), based on $X = \sqrt{4Dt}$						
<i>P</i> (kbar)	<i>T</i> (°C)	<i>t</i> (d)	Fe-Mg Grt (fast)	Fe-Mg Grt (slow)	Ca Grt (slow)	Fe-Mg Px*	Al Cpx	Fe-Mg Ol	Fe-Mg Bt
15	500	120	0.01	<0.01	<0.01	<0.01	<0.01	0.26	0.83
15	500	60	0.01	<0.01	<0.01	<0.01	<0.01	0.19	0.59
15	500	15	<0.01	<0.01	<0.01	<0.01	<0.01	0.09	0.29
15	550	120	0.03	<0.01	<0.01	0.01	<0.01	0.74	2.35
15	550	60	0.02	<0.01	<0.01	<0.01	<0.01	0.53	1.66
15	550	15	0.01	<0.01	<0.01	<0.01	<0.01	0.26	0.83
15	600	60	0.05	0.01	<0.01	0.01	<0.01	1.32	4.17
15	600	30	0.04	<0.01	<0.01	0.01	<0.01	0.93	2.95
15	600	15	0.03	<0.01	<0.01	0.01	<0.01	0.66	2.08
15	700	60	0.28	0.05	0.03	0.08	<0.01	6.25	19.8
15	700	30	0.20	0.03	0.02	0.06	<0.01	4.42	14.0
15	700	15	0.14	0.02	0.02	0.04	<0.01	3.12	9.88
15	800	30	0.76	0.15	0.11	0.28	<0.01	15.7	49.5
15	800	15	0.53	0.11	0.08	0.20	<0.01	11.1	35.0
15	800	7	0.36	0.07	0.05	0.13	<0.01	7.57	23.9
15	900	30	2.28	0.55	0.39	0.99	0.01	44.8	141
15	900	15	1.61	0.39	0.27	0.70	0.01	31.7	100
15	900	7	1.10	0.26	0.19	0.48	0.01	21.6	68.4
15	900	3	0.72	0.17	0.12	0.31	<0.01	14.2	44.8
15	1000	15	4.09	1.15	0.81	2.05	0.03	76.7	242
15	1000	7	2.79	0.78	0.55	1.40	0.02	52.4	166
15	1000	3	1.83	0.51	0.36	0.92	0.01	34.3	109
15	1000	1	1.06	0.30	0.21	0.53	0.01	19.8	62.7
15	1100	7	6.18	1.97	1.40	3.52	0.05	111	353
15	1100	3	4.05	1.29	0.91	2.31	0.03	73.1	231
15	1100	1	2.34	0.75	0.53	1.33	0.02	42.2	133
15	1200	3	8.05	2.88	2.03	5.10	0.07	141	444
15	1200	2	6.57	2.35	1.66	4.17	0.06	115	363
15	1200	1	4.65	1.66	1.17	2.95	0.04	81.1	257
15	1300	2	12.0	4.72	3.34	8.34	0.12	203	642
15	1300	1	8.46	3.34	2.36	5.90	0.08	144	454
15	1400	2	20.3	8.74	6.18	15.4	0.22	335	1060
15	1400	1	14.4	6.18	4.37	10.9	0.16	237	750

Note:  $D(\text{Fe-Mg})\text{Grt}$ , fast = Cygan and Lasaga (1985) with pressure correction of Chakraborty and Ganguly (1991).  $D(\text{Fe-Mg})\text{Grt}$ , slow = Chakraborty and Ganguly (1991).  $D(\text{Ca})\text{Grt}$  = ca.  $0.5 \cdot D(\text{Mg Grt})$ , Chakraborty and Ganguly (1991).  $D(\text{Fe-Mg})\text{Ol}$  = Misener (1974);  $\text{Mg}^* = 0.3$ .  $D(\text{Fe-Mg})\text{Opx}$  = Ganguly and Tazzoli (1994);  $D(\text{Fe-Mg Cpx}) \approx D(\text{Fe-Mg Opx})$  = Ganguly in Ghose and Ganguly (1982).  $D(\text{Al})\text{Cpx}$  = Jaoul et al. (1991).  $D(\text{Fe-Mg})\text{Bt}$  = ca.  $10 \cdot D(\text{Fe-Mg Ol})$  (see text).

\*  $\text{Fe-Mg Cpx} \approx \text{Fe-Mg Opx}$ .

Thus, in experiments in which  $\text{H}_2\text{O}$  has been added to catalyze the reaction, it is likely that the increased rate of reaction represents a transition from a reaction mechanism controlled by lattice diffusion to a much faster interface-controlled solution and precipitation mechanism involving rapid diffusion through the fluid. At the high temperatures at which  $\text{H}_2\text{O}$  reacts with the solid phases to make a melt phase, the melt may also act as an effective intergranular medium for solution and precipitation (e.g., Boettcher and Wyllie, 1968). The effectiveness of even a small amount of moisture as a catalyst is shown by the increase in reaction progress when an experimental mineral mix is exposed to a humid atmosphere or is breathed on (e.g., Boettcher and Wyllie, 1968; Holland, 1980). Vielzeuf and Clemens (1992) noted that tenaciously adsorbed moisture, even in specially dried experimental materials, may be very difficult to drive off entirely, leading to the possibility of some degree of fluxing even in ostensibly unfluxed experiments. In summary, it may be that equilibration by solution and precipitation is more prevalent in experimental solid solution studies than previously thought.

### GARNET + CLINOPYROXENE Fe-Mg EXCHANGE EXPERIMENTS

Below, the apparently reversed experimental data set of Pattison and Newton (1989), reanalyzed by Aranovich and Pattison (1994), on the Fe-Mg exchange between garnet and clinopyroxene is examined in detail to evaluate the extent to which Fe-Mg exchange was the only compositional parameter that varied in the experiments and to assess the relative importance of multicomponent solution and precipitation and diffusion in the experiments (see Tables 1–3 of Pattison and Newton).

#### Experimental details

The starting clinopyroxene compositions in Pattison and Newton (1989) were synthesized along the diopside-hedenbergite join,  $\text{Ca}(\text{Fe,Mg})\text{Si}_2\text{O}_6$ . Microprobe analyses (EDS analysis in Pattison and Newton; WDS analysis in Aranovich and Pattison, 1994) confirmed the expected stoichiometric compositions, with minor heterogeneity (typically <5%). Inserted garnets were synthesized ( $\text{Ca,Fe,Mg})_3\text{Al}_2\text{Si}_3\text{O}_{12}$  solid solutions. Microprobe analy-

ses from both the Pattison and Newton and Aranovich and Pattison studies confirmed that the garnets were close to the expected stoichiometric compositions, although each showed up to 10% heterogeneity.

Garnet and clinopyroxene crystals were inserted as loose grains, 10–50  $\mu\text{m}$  in size, in a garnet : clinopyroxene mass ratio of 95:5 (Method A) or 90:10 (Method B). In hydrothermal experiments between 700 and 1000  $^{\circ}\text{C}$ , the experimental materials were mixed with a small amount of  $\text{H}_2\text{O}$  and oxalic acid hydrate and sealed in Ag capsules. In contrast to the inserted loose mixture of starting materials, the experimental products emerged as variably cemented aggregates of crystals. The extent of cementation increased with temperature. Backscattered electron images of experimental products (Fig. 1 of Aranovich and Pattison, 1994) invariably showed evidence of corrosion and rounding of both garnet and clinopyroxene grains. In experiments at 1100 and 1200  $^{\circ}\text{C}$ , the mineral mixes were dried at 110  $^{\circ}\text{C}$  prior to insertion into graphite capsules. Although no flux was added, the experimental products emerged as cemented pellets, most likely because of a small amount of grain boundary melt that developed in the samples (Aranovich and Pattison, 1994). The source of moisture for the melt may have been atmospheric moisture that entered the mineral mix during insertion into the containers, possibly augmented by residual moisture in the containers or by the penetration of pressure medium material (especially Na).

### Compositions of experimental products

Comparison of averaged microprobe analyses of garnet rims and cores (Pattison and Newton, 1989; Aranovich and Pattison, 1994) showed that, within some scatter, garnet crystals underwent subtle Fe-Mg compositional changes in their rims [ $\Delta\text{Mg}/(\text{Mg} + \text{Fe})$  (core-rim) < 0.03], generally consistent with mass balance constraints (Table 2 of Pattison and Newton and Figs. 2–4 of Aranovich and Pattison). In contrast, clinopyroxene crystals developed rims 5–10  $\mu\text{m}$  wide, even in low temperature experiments (800  $^{\circ}\text{C}$ ), showing substantial compositional changes in all elements including Fe-Mg (Table 2 of Pattison and Newton and Table 1 of Aranovich and Pattison). Final compositions were complex subcalcic clinopyroxene solid solutions bearing Al  $\pm$  Na, contrasting with the starting material of Al-absent, Ca-saturated clinopyroxene.

The textural and compositional observations provide strong evidence that the equilibration mechanism in Pattison and Newton's experiments involved primarily the multicomponent solution and precipitation of both garnet and clinopyroxene, possibly in addition to melting and crystallization processes and minor diffusion in the experiments at 1100 and 1200  $^{\circ}\text{C}$  (see below). The only significant source for Al in the equilibrated clinopyroxene was the volumetrically abundant garnet in the sample. The source of the small and variable amounts of Na detected in the equilibrated clinopyroxenes may have been trace amounts of pressure-medium glass mixed in with

the starting garnet, or possibly Na that diffused through the container material into the experimental sample (Pattison and Newton, 1989; Aranovich and Pattison, 1994). The subtle but generally consistent Fe-Mg shifts in garnet-rim compositions, consistent with mass balance constraints, suggest that clinopyroxene also dissolved and therefore participated in the multicomponent solution and precipitation mechanism.

Evidence for a minor amount of pure Fe-Mg diffusion in clinopyroxene was found only in the experiments at the highest temperature by examining contrasting core-rim profiles of Fe/(Fe + Mg) vs. Al in individual grains containing an Al-bearing rim that mantles an unreacted, Al-free core (Fig. 5). Interpretation of these profiles is complicated by convolution effects (Ganguly et al., 1988), where the excitation volume from microprobe analysis is large compared with the scale of compositional profiles or discontinuities. With the assumption of a finely focused beam diameter of 1  $\mu\text{m}$  and an accelerating voltage of 15 keV, the diameter of the excitation volume for Fe, Mg, and Al for 99% of the X-ray production in clinopyroxene is about 3.0, 4.4, and 4.3  $\mu\text{m}$ , respectively (equations on p. 200–201 of Reed, 1993). Analysis points within about 2.2  $\mu\text{m}$  of the interface between the rims and the seed material (half the diameter of the excitation volume for Mg) may show some smoothing that resembles a diffusion profile but that instead may be due to an overlap of the microprobe excitation volume with material on either side of a sharp discontinuity.

In Figure 5, the solid lines are the inferred locations of the interface between the rim and seed material, located in the interval of maximum slope of the profiles in Al (Ganguly et al., 1988), the slowest diffusing of the elements (see below). The dashed lines 2.2  $\mu\text{m}$  from either side of the solid lines are the limits beyond which the effects of convolution across a sharp discontinuity should cease to be important. In the experiment at 800  $^{\circ}\text{C}$  shown in Figure 5A, all clinopyroxene compositions showing significant Fe-Mg change, compared with the starting Fe-Mg composition, contain significant Al (Fig. 5A). Beyond the limits of the dashed lines, there is no clear evidence of an Fe-Mg diffusional gradient between the seed material and rim, although a very small amount of diffusion (<2  $\mu\text{m}$ ) cannot be ruled out. In contrast, in the experiment at 1200  $^{\circ}\text{C}$  shown in Figure 5B, there is evidence for Fe-Mg gradients in Al-free clinopyroxene 3–4  $\mu\text{m}$  inward from the Al-bearing clinopyroxene rim, suggesting some purely diffusional Fe-Mg exchange between the rim and the seed. This approximate penetration distance is in good agreement with the calculated diffusional profiles discussed below.

In summary, the experiments of Pattison and Newton (1989) provide neither reversals nor unequivocal brackets of the equilibrium clinopyroxene compositions. The criterion of reversibility is undermined in that there is no way to vary pressure or temperature in such a way that the equilibrated grains of subcalcic, Al-bearing, intermediate Fe-Mg clinopyroxene can be returned to their



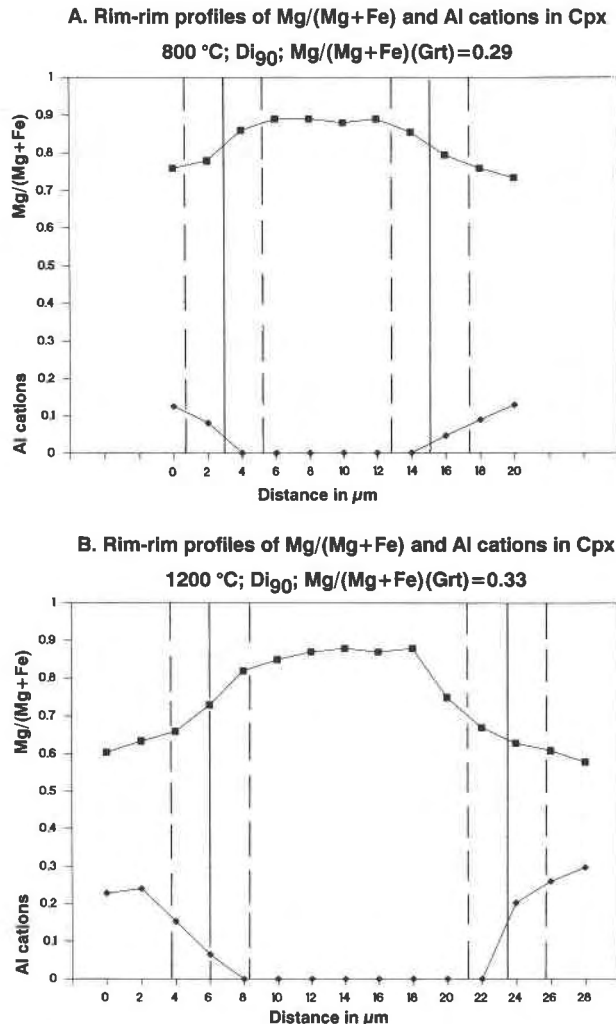


Fig. 5. Rim-to-rim step-scan profiles across two clinopyroxene grains consisting of a central core of unreacted or little-reacted starting material (central part of profiles) mantled by rims of Al-bearing material (marginal parts of profiles) (from Aranovich and Pattison, 1994). The solid lines represent the inferred location of the interface between rim and core, whereas the dashed lines  $2.2 \mu\text{m}$  to either side of the solid lines represent the limits of convolution effects if there were an abrupt compositional discontinuity at the interface. See the text for discussion of the profiles. (A) Expt. 76b(1): 15 kbar, 800 °C, 484 h; starting Cpx- $Di_{90}$ ; starting Grt- $X_{Ca} = 0.2$ , Mg/(Mg + Fe) = 0.43. (B) Expt. 88c: 15 kbar, 1200 °C, 60 h; starting Cpx- $Di_{90}$ ; starting Grt- $X_{Ca} = 0.25$ , Mg/(Mg + Fe) = 0.33.

starting compositions, especially those that are more Fe-rich than the starting garnet. The criterion of bracketing is undermined for two reasons: first, although there is generally an apparent convergence (more correctly a close coincidence) in clinopyroxene Fe-Mg compositions in pairs of experiments using Fe-rich and Mg-rich starting materials, the sense of change in Ca and Al content is unidirectional (the Ca content is always lower, and the Al content is always higher, than in the starting materials,

so that there is no approach from the Ca-poor, Al-rich direction that would be required to provide a bracket); second, the dominance of a solution and precipitation mechanism over a purely diffusional mechanism results in the loss of certainty of the direction to equilibrium from the final measured compositions. This last point is emphasized by some experiments that resulted in compositional overlaps.

#### CALCULATION OF DIFFUSION PENETRATION DISTANCES IN EXPERIMENT TIMES

Table 1 shows calculated diffusion penetration distances for Fe-Mg interdiffusion and some other elements in several minerals for a range of temperatures and experiment times. The diffusion penetration distances were calculated using the expression  $X = \sqrt{4Dt}$  (Crank, 1975), where  $X$  is the diffusion penetration distance,  $D$  is the diffusion coefficient, and  $t$  is time. Appendix 1 shows a sample calculation.

Sources for the experimentally determined diffusion data are listed at the bottom of Table 1. For garnet, the Fe-Mg calculations are based on Mg tracer diffusion data because Mg diffusion is the rate-limiting step in the coupled exchange (Cygan and Lasaga, 1985). The Fe-Mg calculations for slow and fast garnet are based, respectively, on Chakraborty and Ganguly (1991) and Cygan and Lasaga (1985), the latter study incorporating the pressure correction of Chakraborty and Ganguly (1991). Diffusion penetration distances for orthopyroxene are based on the Fe-Mg interdiffusion data of Ganguly and Tazzoli (1994); Fe-Mg interdiffusion in clinopyroxene is expected to be similar to or a little slower than in orthopyroxene (Ghose and Ganguly, 1982; Ganguly, 1993 personal communication). Although there are no experimental Fe-Mg diffusion data for biotite, it is likely from theoretical considerations (Dowty, 1980) that Fe-Mg diffusion is faster in biotite than in olivine, the next-fastest mineral, a view supported by the observation that biotite tends to be unzoned even when olivine in the same rock may be zoned (Ganguly, 1993 personal communication). Thus, biotite Fe-Mg interdiffusion is arbitrarily assumed to be one order of magnitude faster than in olivine.

The calculated values in Table 1 represent the approximate distances into a mineral grain that the diffusion front reaches and should not be confused with the width of a measurable equilibrated rim. Because of convolution effects (Ganguly et al., 1988), measurement of the true rim composition from single-microprobe spot analyses requires a diffusion penetration distance substantially larger than the ca.  $4\text{-}\mu\text{m}$  diameter of the microprobe excitation volume. Ganguly et al. (1988) outlined an approach in which step scans across a diffusion profile can be deconvolved to provide a reasonable estimate of true compositions even when convolution affects individual analyses along the gradient. They noted that, for a step size of  $0.5 \mu\text{m}$  and normal microprobe operating conditions [similar to those used in the studies of Pattison and Newton (1989) and Aranovich and Pattison (1994)], con-

olution effects cease to become significant once the diffusion profile reaches about 15  $\mu\text{m}$  in width.

The calculated values in Table 1 suggest that below 1300 °C for typical experiment times, Fe-Mg diffusion is unlikely to yield a wide enough equilibrated rim in garnet, clinopyroxene, and orthopyroxene to be analyzed with single spot analyses without incorporating a substantial proportion of partially reacted or unreacted material. For olivine and biotite, the corresponding temperature threshold is about 800 °C. The calculated diffusion penetration distances for clinopyroxene are in good agreement with the measured profiles in Figure 5.

The negligible observed and calculated extents of diffusion for the garnet + clinopyroxene experiments of Pattison and Newton (1989) support the conclusion that the process of multicomponent solution and precipitation was the dominant equilibration mechanism in their experiments. Even in their experiments at 800 °C, rim compositions were wide enough to obtain numerous reproducible spot analyses from the edges of single grains. Close coincidence of final compositions from pairs of experiments with substantially different starting Fe-Mg compositions indicates that there was little to no incorporation of unreacted starting material in these analyses, indicating a minimum width of equilibrated material of about 4  $\mu\text{m}$ . On the basis of the calculations in Table 1, such widths would not be expected by Fe-Mg diffusion alone.

Pattison and Newton (1989) interpreted the range of compositions between unreacted starting clinopyroxene and equilibrated rims to represent diffusionally controlled convergence toward equilibrium, the basis for their claim of reversal (i.e., bracketing) of Fe-Mg (but not other elements). Although this explanation is consistent with diffusion, the above considerations suggest that it is more likely that the range of compositions they obtained represent instead mixed analyses from microprobe excitation volumes that incorporated variable proportions of unreacted starting clinopyroxene and equilibrated rims or zones.

## EVALUATION OF OTHER EXPERIMENTAL STUDIES

### Exchange and solid solution experiments

Below, other apparently reversed Fe-Mg exchange and solid solution experiments involving crystalline starting materials are examined to see if equilibration was also achieved by a multicomponent solution-precipitation mechanism and whether the results are truly reversed or unambiguously bracketed. The purpose of this assessment is not to undermine the value of the experiments (see discussion below) but merely to see if the experiments satisfy the strict reversal and bracketing criteria discussed above.

Experiments by Eckert and Bohlen (1992) on the Fe-Mg exchange between garnet and orthopyroxene were conducted using a similar approach to that of Pattison and Newton (1989), with overwhelming abundance of garnet relative to orthopyroxene. In addition to a close

coincidence in Fe-Mg ratio in orthopyroxene from pairs of experiments using Fe-rich and Mg-rich starting compositions, the initially Al-free orthopyroxene took on Al during the experiments. Although Eckert (1994 personal communication) noted complexities in textural and compositional variations in their experimental products that made identification of an equilibration mechanism on observational grounds equivocal, the addition of Al to the initially Al-free orthopyroxene seems to dictate some component of solution and precipitation involving the dissolution of garnet.

Ferry and Spear (1978), in their study of garnet + biotite Fe-Mg exchange, obtained a generally close coincidence of final biotite compositions from paired experiments using Fe-rich and Mg-rich starting compositions in H<sub>2</sub>O-fluxed experiments from 550 to 800 °C, which they interpreted as evidence for reversal (i.e., compositional bracketing). They did not analyze for any elements other than Fe and Mg in biotite, so evidence for multicomponent solution and precipitation in their experiments is difficult to demonstrate. However, the close agreement between pairs of experiments at temperatures as low as 550 °C suggests a solution and precipitation mechanism because diffusion alone at 550 °C for their experiment durations should result in minimal change in biotite and especially garnet (see Table 1). In experiments of similar *P-T* conditions and duration to those of Ferry and Spear, Seifert (1970) noted that stoichiometric phlogopite inserted into H<sub>2</sub>O-fluxed experiments with aluminous phases (Al<sub>2</sub>SiO<sub>5</sub>, cordierite) emerged as Al-bearing eastonitic mica after the experiments, indicating the effectiveness of solution and precipitation in mica recrystallization at these temperatures.

Phase equilibrium experiments by Koziol and Newton (1989) and Koziol (1990) on solution properties of calcium-iron-magnesium garnet, in which a LiMoO<sub>4</sub> flux was used to increase reaction rates, resulted in closely agreeing final garnet compositions from experiments with significantly different starting compositions, which they took as evidence for convergence to equilibrium. They reported equilibrated rims up to 10  $\mu\text{m}$  in width in experiments at 900–1000 °C, for 2–10 d, from which repeated spot analyses gave reproducible results. Examination of Table 1 suggests that, even for fast garnet diffusion, such reproducibility and agreement between experiments using different starting compositions would not be expected from a diffusionally controlled equilibration mechanism alone but more likely are due to solution and precipitation.

Similar arguments apply to the results of Perkins and Vielzeuf (1992) on Fe-Mg exchange between olivine and clinopyroxene. Examination of their Table 4 shows that initially Ca-free olivine took on Ca during the experiments, in addition to changing in Fe/Mg, whereas initially Ca-saturated clinopyroxene became Ca-undersaturated, in addition to changing in Fe/Mg, suggestive of a multicomponent solution and precipitation equilibration process. According to Table 1, their experiments of 3–4 d at 1000 °C would not appear to be long enough to

develop measurable equilibrated rims in clinopyroxene if the equilibration mechanism was Fe-Mg diffusion alone.

Several studies on  $\text{Al}_2\text{O}_3$  solubility in orthopyroxene in equilibrium with garnet (Perkins and Newton, 1980; Lane and Ganguly, 1980; Perkins et al., 1981) obtained good agreement from  $\text{H}_2\text{O}$ -fluxed experiments using Al-rich and Al-poor starting compositions over the temperature range 900–1600 °C and using experimental times ranging from 6 d at 900 °C to 3 h at 1600 °C. The negligible calculated Al-diffusion penetration distances for clinopyroxene (assumed to be similar to orthopyroxene) listed in Table 1 suggest that the equilibration mechanism in these studies involved solution precipitation, a conclusion supported by the occurrence of compositional overlaps in several pairs of experiments (see the discussion above).

In experiments involving phases that show solid solution in only one site (e.g., Na-K exchange between alkali feldspars), the effects of solution precipitation vs. diffusion may be more difficult to distinguish. Goldsmith and Newton (1974), in  $\text{H}_2\text{O}$ -fluxed experiments on the alkali feldspar solvus, obtained close coincidence among experiments whose initial compositions lay inside and outside the solvus over the temperature range 300–600 °C. On the basis of changes in X-ray diffraction patterns, they noted increasing degrees of convergence in progressively longer experiments at the same  $P$ - $T$  conditions, which they ascribed to continuous compositional change toward the equilibrium composition, and hence evidence for reversal (compositional bracketing). Given the very low temperatures of some of their apparent convergences, however, diffusion rates (Yund, 1983) would most likely be too slow to effect these changes. An alternate interpretation is that the final equilibrated compositions grew at the expense of the starting compositions that were out of equilibrium by a solution and precipitation mechanism, with the increasing degrees of apparent convergence with time representing increasing degrees of reaction progress.

### Stable isotopic exchange experiments

The issue of equilibrium bracketing in stable isotopic exchange experiments has been discussed by Chacko (1993) and O'Neil (1986). Chacko noted that, for the same reasons discussed in this paper, strict isotopic reversals using a convergence approach (similar to that described above for cation exchange experiments) are unlikely because of the negligible expected diffusion penetration distances for the experiment times involved. Both authors noted that experiments involving recrystallization of crystalline starting materials in fluxed experiments are preferable to synthesis experiments from gels or oxide mixes, although neither method provides an unequivocal bracket of the equilibrium isotopic fractionation (both processes involve either solution or precipitation or both).

### IMPLICATIONS FOR SOLID SOLUTION EXPERIMENTS

The above survey represents a sampling of solid solution experiments using crystalline starting materials. Reversals (meaning apparent compositional convergences)

were inferred from the close agreement among experiments using different starting materials. Because the equilibration mechanism in most, if not all, cases probably involved a multicomponent solution and precipitation mechanism, sometimes with no possibility of returning the final compositions to the starting compositions and typically involving variation in several compositional parameters, the experiments, strictly speaking, cannot be regarded as truly reversed or bracketed.

These conclusions, although seemingly negative, are not intended to undermine the value of solid solution experiments that use crystalline starting materials or as justification for crystallization and synthesis experiments that use disordered, high free-energy starting materials such as glass, gels, or oxide mixes. First, in experiments using crystalline starting materials, the inserted phases are of the same structure and generally of similar composition to the final products. This results in a smaller free-energy difference between the starting material and the final products than between glass, gels, and oxides and final products, which in turn reduces the possibility of jumping to grossly metastable final compositions compared with synthesis experiments (see the discussion in Chacko, 1993, p. 362).

Second, there are many reasons to suggest that experiments using crystalline starting materials, although possibly unreversed and unbracketed, result in a close approach to equilibrium and provide high-quality data. Excellent agreement and generally minimal overlap between pairs of experiments that started from opposing compositional directions suggest that the equilibrium composition lies within the range bounded by the measured final compositions and their analytical uncertainties. Smooth, consistent compositional variations in pressure, temperature, and other compositional parameters are suggestive of a close approach to equilibrium. Highly reproducible results from the same starting materials for different experiment times and using different experimental techniques (e.g., Pattison and Newton, 1989; Perkins and Vielzeuf, 1992) further suggest a close approach to equilibrium. Finally, consistent thermodynamic data have been extracted from redundant sets of experiments: Berman et al. (1994) extracted thermodynamic data for garnet, clinopyroxene, and olivine that satisfy individual studies on garnet + clinopyroxene, olivine + clinopyroxene, and garnet + olivine.

Nevertheless, use of the terms reversal and compositional bracket to describe apparent convergence experiments that equilibrated by a solution and precipitation mechanism, especially those involving variation in more than one compositional parameter, should be abandoned in favor of the terms consistency experiment or redundancy experiment, which emphasize the increased degree of confidence in an experimental result when it is achieved using different starting materials or starting compositions. In diagrams showing compositional changes in experiments, the use of solid arrows connecting starting compositions to final compositions like B and C in Figure 2, which give the impression of continuous change, should

be replaced with nondirectional symbols connecting initial and final compositions like D in Figure 2.

### IMPLICATIONS FOR THERMODYNAMIC DATA EXTRACTION

The above considerations carry implications for techniques for extracting thermodynamic data and mixing properties from solid solution experiments involving crystalline starting materials. The free-energy inequality techniques of Gordon (1973) and Berman et al. (1986) rely on free-energy brackets to constrain possible solutions. This approach, initially developed to treat reversal brackets of univariant equilibria involving phases of fixed composition, can be extended to solid solution experiments, provided that unequivocal compositional brackets are obtained and are assumed to be equivalent to reversal brackets.

However, because most solid solution data are probably not truly reversed or bracketed, many apparent half-brackets, strictly speaking, can no longer be treated as limiting. In pairs of experiments starting from opposing compositional directions, the equilibrium compositions must have lower free energy than the starting compositions and as such must lie between compositional brackets defined by the starting compositions. In contrast, the final compositions themselves cannot be interpreted as limiting compositional brackets, even though they may indeed represent a close approach to equilibrium (see the discussion above and Fig. 4B).

One solution to this problem is to assume that, in pairs of experiments starting from opposing compositional directions, the equilibrium composition probably lies somewhere in the range defined by the final measured compositions plus their analytical uncertainties, allowing the assignment of effective (but not strictly limiting) brackets (Berman et al., 1994). Nevertheless, without unambiguous knowledge of the direction to equilibrium from the final compositions, least-squares regression of (assumed) equilibrium compositions (e.g., Powell and Holland, 1985) is an equally justifiable means of treating experimental solid solution data. Both techniques require qualitative judgment in the rejection of outliers. Perkins and Vielzeuf (1992), in applying both techniques to their experiments on Fe-Mg exchange between clinopyroxene and olivine, achieved essentially identical results, suggesting that both approaches are satisfactory in extracting thermodynamic data from solid solution experiments.

### ACKNOWLEDGMENTS

This research was supported by NSERC operating grant 037233. I thank T. Chacko for providing the impetus to calculate diffusion penetration distances for experiment times and T.M. Gordon for clarifying my thinking on reversibility vs. compositional bracketing. The paper was improved by the thoughtful reviews of R.G. Berman, E.D. Ghent, A.M. Koziol, and especially J.O. Eckert and D. Perkins III. In addition to those named above, I acknowledge stimulating discussions with L.Ya. Aranovich, J. Farquhar, J. Ganguly, S.L. Harley, R. Joesten, and R.C. Newton on solid solution experiments. All errors or misconceptions are my own.

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MANUSCRIPT RECEIVED SEPTEMBER 21, 1993

MANUSCRIPT ACCEPTED MAY 5, 1994

#### APPENDIX 1. SAMPLE CALCULATION OF A DIFFUSION PENETRATION DISTANCE

The diffusion penetration distance for Fe-Mg interdiffusion in garnet at 1000 °C for a 7-d experiment is calculated below using the experimental data for Mg tracer diffusion of Chakraborty and Ganguly (1991). Their expression for the calculation of the diffusion coefficient is as follows:

$$D^*(P) = D_0 \cdot \exp\{-Q + (P - 1) \cdot \Delta V^+ / RT\}$$

where  $D^*(P)$  is the tracer diffusion coefficient at pressure  $P$  (bars) and temperature  $T$  (K),  $D_0$  is the preexponential factor,  $Q$  is the activation energy at 1 bar, and  $\Delta V^+$  is the activation volume. From Table 1 of Chakraborty and Ganguly, the values for the above parameters for Mg<sup>2+</sup> are  $D_0 = 2.79 \times 10^{-4}$  cm<sup>2</sup>/s;  $Q = 65457$  cal/mol;  $\Delta V^+ = 0.078$  cal/(bar·mol);  $R = 1.98726$  cal/(mol·K); and  $T = 1000 + 273 = 1273$  K. This results in a value of  $D^*(P)$  at 1000 °C and 15 kbar (15000 bars) of  $2.57 \times 10^{-15}$  cm<sup>2</sup>/s, or a value of  $\log_{10} D^*(P)$  of  $-14.6$  cm<sup>2</sup>/s.

The expression for diffusion penetration distance (Crank, 1975) is

$$X = \sqrt{4Dt}$$

where  $X$  is the penetration distance,  $D$  is the diffusion coefficient calculated above, and  $t$  is time. For a 7-d experiment,  $t = 7 \times 24 \times 60 \times 60 = 6.05 \times 10^5$  s. This results in a value for  $X$  of  $7.8 \times 10^{-5}$  cm, or 0.78 μm.