

## Experimental determination of univariant equilibria using divariant solid-solution assemblages: a reply

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### Introduction

Boettcher's discussion does not, in our opinion, contain any arguments which invalidate the method described in our original paper (Schmid *et al.*, 1978). His comments do, however, indicate that there is some need for clarification of the "solid-solution" method and we will take the opportunity to elaborate this reply accordingly. Boettcher's comments may be summarized under the following headings, and we will consider them in the order we list them.

1. Uncertainties in the composition of the solid solution generate uncertainties in the calculated position of the end-member reaction.

2. The assumption of an ionic solution model with Raoult's Law behavior for  $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$  component in  $(\text{Ca}_{0.978}\text{Fe}_{0.022})\text{Al}_2\text{Si}_3\text{O}_{12}$  garnet may be in error.

3. In some cases the "solid-solution" method is irrelevant because the conventional "modal" approach is as precise as the high-pressure apparatus allows.

4. More than one of the phases present may be a solid solution.

5. Our statement that small amounts of an additional component (in this case  $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ ) increases reaction rates is erroneous.

The basis of the solid solution method as applied to the reaction:



is illustrated in Figure 1, which has been constructed, at constant temperature, on the assumption that gar-

net is the only solid solution. The essence of the method is to use a mixture of crystals of anorthite, kyanite, quartz (all pure), and a garnet solid solution which is close in composition to grossular. We have used  $\text{Gr}_{97}\text{Alm}_3$  as an example. We then attempt to bracket the equilibrium pressure ( $P_2$ ) for coexistence of the solid solution and the other three phases. To do this it is necessary to make a run at some pressure  $P_1$  and to establish that anorthite is breaking down. A run which indicates anorthite growth at  $P_3$  brackets the equilibrium pressure  $P_2$ . Conventionally, the "modal" method would require demonstration of substantial anorthite growth at  $P_3$  and substantial garnet growth at  $P_1$ . However, all that is required in our proposed method is that the garnet cell edge indicates increasing grossular content at  $P_1$  and decreasing grossular content at  $P_2$ . Thus the equilibrium pressure for  $\text{Gr}_{97}\text{Alm}_3$  is bracketed by shifts in phase composition. It is *not* necessary (as implied by Boettcher) to obtain unzoned crystals of accurately known composition at  $P_1$  and  $P_3$ . A small change in average composition as indicated by a shift in average cell edge is sufficient to indicate the direction of reaction. Figure 2 illustrates the relationship between the changing composition of garnet and the amount of this phase present in "solid-solution" experiments. If a garnet of initial composition  $\text{Gr}_{97}\text{Alm}_3$  were used, then in order to change its proportion by a detectable amount (30% or so), a change in net composition of about 0.01 mole fraction would be required. In some of our solid-solution runs compositional changes of this order were observed (Table 1 in our paper), and

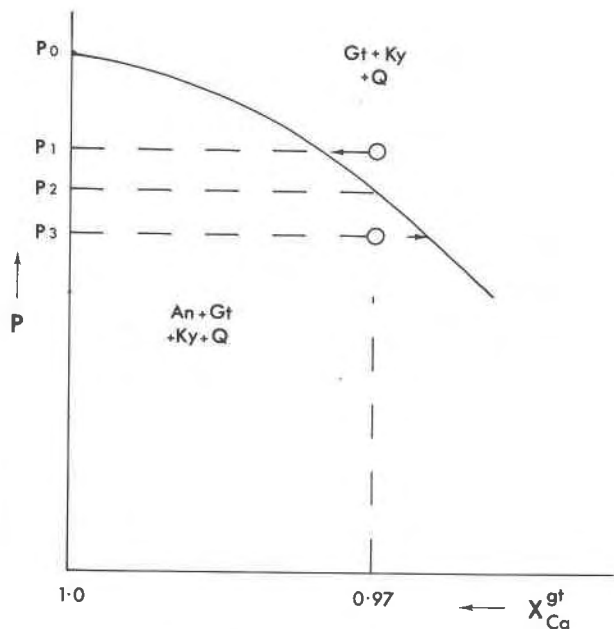


Fig. 1. A garnet solid solution of  $X_{Gr} = 0.97$  would be in equilibrium with anorthite, kyanite and quartz at  $P_2$ . This pressure is experimentally bracketed by demonstrating increasing  $X_{Ca}^{gt}$  at  $P_1$  and decreasing  $X_{Ca}^{gt}$  at  $P_3$ .

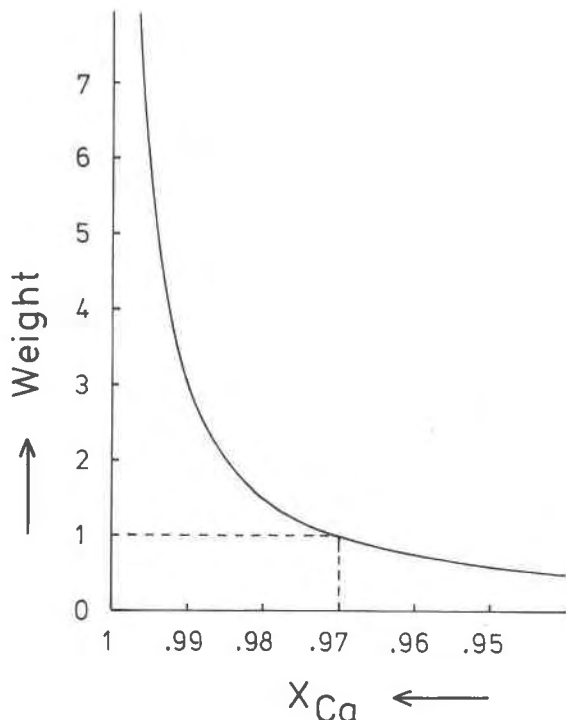


Fig. 2. The relationship between weight of garnet and its composition in a closed system consisting of garnet, anorthite, kyanite, and quartz. For an initial unit amount of garnet of composition  $X_{Ca}^{gt} = 0.97$ , the amount present will follow the illustrated curve as its bulk composition changes.

they did correspond with demonstrable changes in proportions of phases. Changes of amounts of phases may of course be used to validate and complement observed compositional shifts. The smallest detectable change in garnet composition ( $X_{Gr} \approx 0.002$ ) is, however, very much smaller than the smallest detectable change in proportion of garnet present. Hence the solid-solution method is potentially much more sensitive than the conventional approach.

Having bracketed the equilibrium pressure for the garnet solid solution, we may determine the equilibrium pressure for the pure phases,  $P_0$ , by applying the relationship:

$$P_0 - P_2 = \Delta P = \frac{3RT}{\Delta V^0} \ln X_{Gr} \quad (2)$$

This assumes random mixing of three Ca and Fe atoms per formula unit and Raoult's Law behavior of the grossular component. In the absence of charge-balance constraints of the type present in plagioclase (NaSi substituting for CaAl, see Kerrick and Darken, 1975), it is extremely unlikely that the Ca and Fe atoms do not mix on an ionic basis. Indeed, the garnet structure requires Ca-Fe mixing rather than  $Ca_3Al_2Si_3O_{12}$ - $Fe_3Al_2Si_3O_{12}$  'molecular' mixing. The standard state chosen for grossular necessitates of course that Raoult's Law is approached as  $X_{Gr}$  approaches 1. Any deviation from ideality at  $X_{Gr}$  of 0.978 must therefore be extremely small. In additional support of our assumption of ideal three-site mixing, Hensen *et al.* (1975) have found near-ideal three-site mixing for Mg-rich grossular-pyrope garnets and Cressey *et al.* (1978) found near-ideal 3-site mixing for the grossular-almandine series used here. For the values of  $\Delta P$  obtained in our study (up to 0.21 kbar), errors could not conceivably be greater than 20-30% of  $\Delta P$  from this source, and uncertainties closer to 0.01 kbar (5 percent) are much more likely.

The reaction chosen to illustrate the solid solution method is extremely sluggish if all the phases are pure, so that any method which requires only a very small extent of reaction is of great usefulness. Boettcher points out however that for reactions such as:



the solid-solution approach is no advance on the conventional one, because this reaction takes place very rapidly at low temperatures in the presence of  $H_2O$ . We agree that in this and many other cases there is

no particular reason to use the solid-solution method, and would not suggest that it replace the "modal" approach in the study of such reactions. Unfortunately, however, not all reactions take place as readily as reaction (3), so Boettcher's comment is not really germane to our discussion. The important point is that the solid-solution method is a useful tool for the experimentalist concerned with very sluggish reactions which cannot be precisely bracketed by conventional methods. It is intended to complement rather than replace other methods of study.

If one of the phases other than garnet is turned into a solid solution by adding  $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$  component, then, as discussed by Boettcher, equation (2) would need to be modified to take account of the composition of this second phase. Boettcher suggests that  $\text{Fe}^{2+}$  may substitute for Ca in anorthite, producing an error in our calculation of  $P_0$ . All the available evidence indicates, however that the extent of any such substitution must be extremely small under the conditions of our experiments. For example Sen (1960) found only 0.12 wt.% Fe in  $\text{An}_{42.5}$  plagioclase coexisting with garnet in an iron-rich (11 wt.% Fe) granulite. Analyses of anorthite crystals produced in a number of our experiments indicate that the extent of Fe substitution for Ca in this phase is less than 1/6 that in coexisting garnet, and probably nearer to 1/20. These analyses were performed with an electron microprobe and with an AEI electron microscope microanalyzer (EMMA IV) on anorthite coexisting with Fe-rich garnet, quartz, and an aluminosilicate polymorph. Bearing in mind the problems of analyzing small overlapping crystals, the ratio 1/6 is almost certainly a large overestimate but, even if correct, it would only shift the calculation of  $P_0$  down by 0.03 kbar. This is within the gauge reading error for most piston-cylinder experiments.

The observation that addition of a few mole percent of another component tends to enhance recrystallization rates is commonly but not universally made in ceramic systems. A considerable amount of work has been done on MgO (e.g. Layden and McQuarie, 1959), and it has been found that elements such as Fe, Ti, and V, which have more than

one stable oxidation state, increase the rate at which the MgO recrystallizes. This may be due to their contribution of small amounts of vacancies which promote volume diffusion and/or to the production of a reactive grain boundary layer. In either case we see no reason why similar principles should not apply to silicate solid solutions. Hence the statement made in our paper.

In conclusion, we believe that our "solid-solution" method will prove to be very useful in the experimental determination of sluggish univariant reactions. In the example we have used, the combined uncertainties due to adding Fe-components are less than 0.07 kbar in the calculated position of the end-member reaction. For experiments performed in the piston-cylinder apparatus this is less than the reproducibility of the experimental conditions and is hence perfectly acceptable. It is also an acceptable uncertainty in cases where reactions cannot be bracketed to within less than a few hundred bars by the "modal" method. Boettcher's discussion, and this reply, serve however to highlight the points over which care must be taken when extra components are added.

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