

Activity-Composition Relationships for Pyrope-Grossular Garnet

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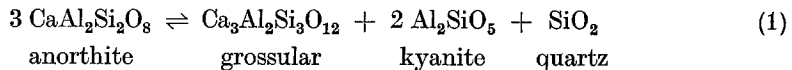
Abstract. Activity coefficients (γ) for grossular in pyrope-grossular garnet have been determined experimentally using the divariant assemblage garnet-anorthite-sillimanite (kyanite)—quartz. Values of γ for garnets with 10–12 mole % grossular have been obtained at 1000°, 1100°, 1200° and 1300° C at pressures between 15 and 21 Kb. The data are consistent with a symmetrical regular solid model for grossular-pyrope solid solutions. The interaction parameter (W) increases linearly with decreasing temperature and is given by $W = 7460 - 4.3 T$ cals (T in °K). A solvus in the pyrope-grossular solid solution is predicted with a temperature of critical mixing of 629° C \pm 90° C.

Introduction

The mixing properties of garnet solid solutions have been discussed by various authors (*e.g.* Saxena [1], Ganguly [2], Wood [3]) but no quantitative experimental data have been available to date. In view of the potential of garnet bearing assemblages as indicators of pressure-temperature (PT) conditions of metamorphism, a better understanding of the composition-activity relationships in garnets is of major interest.

In the present paper we report an experimental study of the activity of grossular component in pyrope-grossular garnet at high pressure and temperature.

Using the end member reaction



the activities of $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ component in Ca—Mg garnets in the assemblages garnet_{ss}—anorthite—kyanite—quartz and garnet_{ss}—anorthite—sillimanite—quartz can be calculated at a range of pressures and temperatures from the relationship

$$(P_0 - P_1) \Delta V_0 = RT \ln a_{\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}}^{gt} \quad (2)$$

where P_0 is the equilibrium pressure for reaction (1) at the temperature of interest (T in °K), ΔV_0 is the volume change of reaction (1) at room temperature, P_1 is the pressure of interest, $a_{\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}}^{gt}$ is the activity of grossular component in the pyr-

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ope-grossular solid solution and R is the gas constant¹. By determining garnet compositions at various temperatures and pressures the activity coefficient for grossular component can be obtained from the relation for 3-site Mg—Ca mixing:

$$a_{\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}}^{\text{gt}} = (X_{\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}} \gamma_{\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}})^3$$

where $X_{\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}}$ is the mole fraction of grossular component in the garnet solid solution and $\gamma_{\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}}$ is the activity coefficient of grossular in the garnet solid solution.

Assuming the garnet to be a symmetrical regular solution (Thompson, [4] the interaction (or Margules) parameter (W) can be calculated by

$$W = \frac{RT \ln \gamma_{\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}}}{(1 - X_{\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}})^2} \quad (3)$$

and the critical temperature of mixing is given by

$$T_c = \frac{W}{2R} \quad (4)$$

The anorthite breakdown reaction (1) is well known from the work of Hays [5], Hariya and Kennedy [6] and Newton [7]. Because the accuracy of the activity data depends critically on the position of the anorthite reaction boundary a check on this boundary has been carried to ensure internal consistency of the data used to calculate the activity coefficients.

Experimental Technique

The experiments were carried out in conventional, $\frac{1}{2}$ inch, Boyd and England [8] type piston cylinder apparatus, using talc and boron-nitride as pressure media.

Temperatures were controlled to within 5° C of the quoted values using *Pt/Pt*—13% *Rd* thermocouples.

The 'hot piston out' procedure was used throughout; the run is taken to a pressure 5 kb in excess of the desired value and taken to temperature before the pressure is brought back to the final value. Pressures reported are uncorrected values. The apparatus has been calibrated with respect to other laboratories at 1200° and 1300° C and 15–20 Kb and very good agreement with previously published data has been found (Hensen and Barton [9]).

Starting materials were run in unwelded *Pt*-capsules. Samples were moistened by breathing for runs at 1000° and 1100° C. Run times were around 1 hr at 1300° C, 5 hrs at 1200° C and varied from 17–25 hrs at 1000° and 1100° C.

The material used in the experiments consisted of 55% of a glass of composition anorthite₅₀ ensatite₅₀ (molar) plus 27% sillimanite (Brandewyne Springs, Del. by courtesy of Dr. P. M. Bell) and 18% excess purified quartz. This mixture was seeded with 4–8% garnet bearing high pressure assemblage to provide the starting material for most runs. A reversal using crystalline starting materials only has also been carried out.

In view of the fact that consistent, reproducible and, as demonstrated in one instance, reversible data could be obtained it is believed that equilibrium was closely approached in the experimental runs.

All runs were checked optically and by powder X-ray photography to ensure they contained the full mineral assemblage of interest. This is of major importance as it is not unusual at temperatures of 1200° C and above for quartz or anorthite to disappear owing to partial melting. In such cases the garnet composition is no longer fixed and cannot be used for the determination of activity coefficients.

¹ Standard states for all components are taken to be the pure phases at the pressure and temperature of interest.

Table 1. Run data and garnet composition in the assemblage garnet-anorthite-sillimanite-quartz

| Run No. | Temp. (°C) | Press. (Kb) | Cell edge ^b a_0 (Å) | Garnet composition (mole fraction of grossular component) | | γ^a | W (cals) |
|-----------------|------------|-------------|----------------------------------|---|------------|------------|------------|
| | | | | X-ray | microprobe | | |
| 94 | 1300 | 16 | 11.502 | 0.11 | 0.11 | 1.154 | 565 |
| 78 | 1300 | 21 | 11.544 | 0.22 | | 1.153 | 731 |
| 67 | 1200 | 15 | 11.497 | 0.10 | 0.11 | 1.353 | 1092 |
| 81 | 1200 | 16.5 | 11.507 | 0.12 | | 1.408 | 1293 |
| 88 | 1200 | 18.5 | 11.530 | 0.18 | | 1.260 | 1006 |
| 101 | 1200 | 19 | 11.534 | 0.19 | 0.19 | 1.287 | 1126 |
| 65 | 1100 | 15 | 11.503 | 0.11 | 0.11 | 1.554 | 1581 |
| 77 | 1100 | 17.3 | 11.523 | 0.16 | 0.16 | 1.527 | 1637 |
| 83 | 1100 | 18.5 | 11.541 | 0.21 | | 1.418 | 1527 |
| 80 | 1000 | 17 | 11.537 | 0.20 | 0.20 | 1.656 | 1994 |
| 85 ^c | 1000 | 17 | 11.547 | 0.22 | | 1.574 | 1886 |

^a See introduction for definition of symbols.

^b Accuracy in a_0 measurement is better than 0.005 Å.

^c In this run kyanite occurs instead of sillimanite.

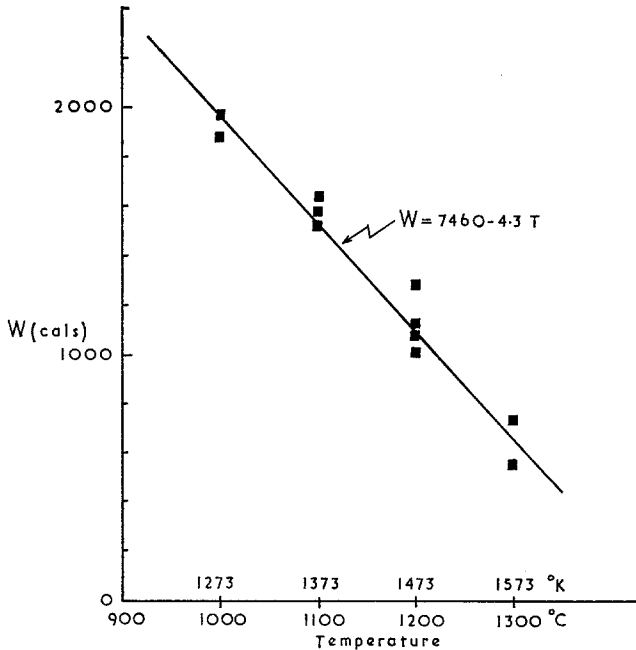


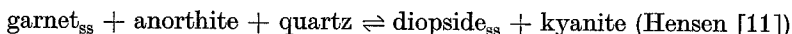
Fig. 1. Plot of the interaction parameter (W) against temperature. A linear least squares fit to the data is shown on the diagram

Experimental Data

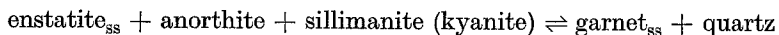
The experimental results are given in Table 1 and Fig. 1 shows a plot of the calculated interaction parameter W against temperature. The grossular content of

the garnet in the assemblage garnet-anorthite-sillimanite-quartz has been determined from cell edge measurements obtained from X-ray powder photographs. In addition electron microprobe analyses of a number of runs have been carried using the TPD probe with non-dispersive detection system. (Reed and Ware [10]). The results of these analyses agree well with the X-ray data (Table 1). However the microprobe revealed that compositions approximating the seed composition ($X_{\text{Gross}} \approx 0.21$) sometimes persist in cores in garnets of the composition indicated by the X-ray data. This shows that although garnet of a certain composition grows from the fine grained low pressure assemblage (that forms from the glass on heating) the rate of diffusion within garnet is too low to allow complete equilibration between cores and rims.

The reason that no data are reported above 17 Kb at 1000° C and 21 Kb at 1300° C is that above these pressures the assemblage garnet—anorthite—kyanite—quartz is no longer stable owing to the univariant reaction



At low pressure the assemblage of interest is limited by the reaction



Experimental data on these reactions will be published shortly (Hensen [12])

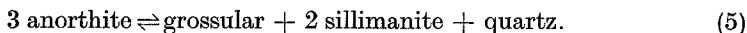
Several experimental runs in Table 1 have the assemblage garnet—anorthite—sillimanite—quartz though they crystallised in the kyanite stability field. The fact that these experimental assemblages are metastable does not affect their usefulness for the activity calculations. This is well illustrated by two runs at 1000° C — 17 Kb (Table 1) one of which was seeded with kyanite². The calculated interaction parameter (W) is the same, within experimental error, for the latter run (assemblage garnet—anorthite—kyanite—quartz) as for the former (assemblage garnet—anorthite—sillimanite—quartz). This also is good evidence that the results represent equilibrium data.

The garnet compositions obtained experimentally were compared with the activities, calculated using expression (2), and the resulting activity coefficients are shown in Table 1. The following data were used to calculate the activities of grossular component in pyrope grossular solid solution.

- a) The anorthite breakdown curve (1) according to Hariya and Kennedy [6].

$$\Delta V_0 = 66 \text{cc. The reaction is given by } P = -1200 + 23.3T \quad (P \text{ in bars, } T \text{ in } ^\circ\text{C}).$$

- b) The equivalent metastable reaction



$$\Delta V_0 = 54.4 \text{ cc; } P = -460 + 24.2T \quad (P \text{ in bars, } T \text{ in } ^\circ\text{C}).$$

The expression for this reaction was calculated using the following data for the kyanite-sillimanite phase boundary

$$\Delta V_0 = 5.8 \text{cc; } P = -6500 + 21T \quad (P \text{ in bars, } T \text{ in } ^\circ\text{C}).$$

These data for the kyanite-sillimanite boundary are consistent with the piston out data of O'Hara and Richardson [13] and the hydrostatic data of Richardson *et al.* [14]. A reversal on this boundary in our apparatus at 1300° C gave a value of 20.5 ± 0.5 Kb in excellent agreement with O'Hara and Richardson [13] (Hensen and Barton [9]).

² The starting material for this run consisted of garnet—clinopyroxene—kyanite—sillimanite—
anorthite—quartz.

A reversal of the anorthite breakdown curve (1) at 1300° C gave a value between 29 and 29.5 Kb agreeing well with the value of 29.1 given by Hariya and Kennedy [6].

The interaction (or Margules) parameters are also given in Table 1. The values obtained at each temperature show minor random variation, which can be attributed to experimental error, and are consistent with a symmetrical regular solution model, *c.f.* Thompson [4]. In view of the fact that only a relatively small range of garnet compositions could be studied (reasons given above) the possibility of asymmetry in the pyrope-grossular solvus cannot be excluded. A significant near linear temperature dependence of W is evident from the data. A least Squares fit of the data gives $W = 7460 - 4.3T$ cals (T in °K). As shown in figure 1 the data fit this linear equation remarkably well.

Discussion of Errors

The internal consistency of the data is very good. Uncertainty in the ΔP values in Eq. (2) is the main possible source of error for the W values. At 1000° C a pressure uncertainty in ΔP of 0.25 Kb has a corresponding error in W of around 10%. The checks carried out on the anorthite breakdown curve (1) and the kyanite-sillimanite phase boundary, mentioned above, give confidence that the error due to the uncertainty in ΔP is small, perhaps in the order of 5–10%.

Errors due to uncertainties in garnet composition are relatively small. The uncertainty of ± 0.01 in the mole fraction of the grossular component resulting from an error of $\pm 0.005 \text{ \AA}$ in the cell edge measurements produces an error in W of about 4%. Compounded error in W is believed to be better than 10%.

Conclusions

The experimental data demonstrate that pyrope-grossular solid solutions exhibit a significant positive deviation from ideality that increases with decreasing temperature. Assuming a symmetrical regular solution the interaction parameter is given by $W = 7460 - 4.3 T$ cals (T in °K). The temperature of critical mixing (T_c), marking the top of the pyrope-grossular solvus, equals $629 \pm 90^\circ \text{ C}$ (assuming a 10% error in W).

A critical temperature of 629° C is consistent with recent experimental data on univariant reactions in the system CaO-MgO-Al₂O₃-SiO₂ (Hensen [12]) that indicate a solvus temperature above 600° C.

The present data are consistent with those presented by Ganguly and Kennedy for a temperature close to 600° C. They give an approximate value of $W \approx 3.8 \pm 0.2$ K cals that is independent of temperature. Ganguly and Kennedy [2] predict a critical temperature of $694 \pm 55^\circ \text{ C}$ which overlaps with the present estimate of $629 \pm 90^\circ \text{ C}$. The reason that coexisting garnets are unknown from natural occurrences (or experiments for that matter) lies in the fact that other, mainly hydrous, phase assemblages replace Ca-Mg garnet at temperatures below 750–800° C.

More information on the mixing properties of almandine-grossular and almandine-pyrope will be required before the present data can be quantitatively applied to natural rocks.

Preliminary results by Cressey (personal communication) indicate near ideality for almandine-grossular solid solution in agreement with the estimate of Ganguly

and Kennedy [2]. In contrast with Ganguly and Kennedy we believe pyrope-almandine garnets are not likely to depart greatly from ideality (Wood [3]) such that the pyrope-grossular interaction parameter may be the only significant factor to be considered when dealing with 3 component Ca-Fe-Mg garnets.

In natural rocks the coexisting plagioclase commonly contains an appreciable amount of albite solid solution. The mixing properties of albite-anorthite solid solutions are incompletely known as yet but the data of Orville [15] can be tentatively used, *c.f.* Schmid and Wood [16].

It is hoped that in the near future the mixing properties of garnets, pyroxenes, feldspars etc. will receive extra attention and that this paper will stimulate such research.

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